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National Inventory of Natural Sources and Emissions of Nitrogen Compounds

Economic and Technical Review
Report EPS 3-AP-80-4

Air Pollution Control Directorate
January 1981

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**NATIONAL INVENTORY OF NATURAL SOURCES AND EMISSIONS
OF NITROGEN COMPOUNDS**

Pollution Data Analysis Division
Air Pollution Programs Branch
Air Pollution Control Directorate

Report EPS 3-AP-80-4
January 1981

Prepared for Environment Canada by the Environmental Applications Group Limited,
Toronto, Ontario, under Department of Supply and Services Contract No. 0SS79-0086.

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Cat. No. En 42-3/80-4E
ISBN 0-662-11383-7

ABSTRACT

Among the more important nitrogenous compounds emitted into the atmosphere from natural sources are nitrous oxide (N_2O), nitrogen oxide compounds (NO_x), ammonia (NH_3) and aliphatic amines. Principal emitting sources are soils and marine waters for N_2O , soils and lightning for NO_x , soils and animal wastes for NH_3 , and animal wastes for aliphatic amines. Nitrogen oxides emitted from fires are less important.

This report provides a first approximation of Canadian emissions of nitrogenous compounds from natural sources. The estimates presented are frequently calculated from a limited data base, thereby requiring application of a number of assumptions and extrapolations. All fluxes should consequently be regarded as order of magnitude approximations.

Emissions data are presented for each Canadian province using fluxes estimated from Canadian soil orders and various biome components. To facilitate this procedure, areas of the different soil orders and biomes were computed for each census division. Marine regions were separated into four sections, two for the Atlantic and one for each of the Pacific and Arctic regions.

Annual emissions of N_2O , NO_x and NH_3 from Canadian terrestrial geographic zones are broadly comparable, and were estimated on a nationwide basis at 732×10^6 kgN, 819×10^6 kgN and 471×10^6 kgN, respectively. Eastern Canada and the two Territories showed a dominance of N_2O and NO_x production over that of NH_3 , whereas Western Canada showed the reverse. Emissions of amines were considerably less than those of other principal nitrogen compounds. N_2O was the only nitrogenous compound emitted in appreciable quantities from marine environments. Ratios of N_2O , NO_x and NH_3 emissions determined in this study were similar to published global ratios.

Also included in this report are data and discussions pertaining to atmospheric concentrations, lifetimes and atmospheric fates of N_2O , NO_x , NH_3 and amines.

RÉSUMÉ

On compte au nombre des principaux composés azotés émis par des sources naturelles l'oxyde de diazote (N_2O), les oxydes d'azote (NO_x), l'ammoniac (NH_3) et les amines aliphatiques. Pour le N_2O , les principales sources d'émission sont les sols et les eaux marines, pour les NO_x , les sols et la foudre, pour le NH_3 , les sols et les déchets animaux et pour les amines aliphatiques, les déchets animaux. La quantité d'oxydes d'azote dégagée par les incendies est de moindre importance.

Le présent rapport donne une première estimation des émissions naturelles des composés azotés au Canada. Les données de base utilisées sont souvent peu nombreuses, d'où la nécessité de recourir à un certain nombre d'hypothèses et d'extrapolations. Il faudrait par conséquent considérer tous les chiffres sur les émissions comme des approximations.

Les données sur chaque province ont été établies à partir de l'évaluation des émissions provenant des ordres des sols du Canada et des divers composants des biomes. Pour faciliter les calculs, on a compilé, pour chaque division du recensement, des données sur diverses zones des biomes et des ordres des sols. On a subdivisé les régions maritimes en quatre parties: deux pour l'Atlantique, une pour le Pacifique et une pour l'Arctique.

Dans les régions terrestres du pays, les émissions annuelles de N_2O , de NO_x et de NH_3 sont largement comparables à l'échelle nationale et sont estimées respectivement à 732×10^6 kgN, 819×10^6 kgN et 471×10^6 kgN. Les émissions de NO_2 et des NO_x sont supérieures dans l'Est et les Territoires à celles du NH_3 ; dans l'Ouest, on observe le contraire. Les émissions d'amines sont beaucoup moins considérables que celles des autres composés azotés. Le N_2O est le seul composé azoté à provenir de milieux marins en quantité remarquable. Les proportions établies dans cette étude entre les émissions de N_2O , de NO_x et de NH_3 se comparent aux proportions globales déjà publiées sur le sujet.

Le rapport contient aussi des données et des discussions sur la concentration, la durée de vie et le devenir dans l'atmosphère des composés N_2O , NO_x , NH_3 et des amines.

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1 INTRODUCTION AND STUDY OBJECTIVES

A principal objective of Environment Canada's Long-Range Transport of Air Pollutants (LRTAP) Program is the development of the capability to assess and predict present and future distributions and depositions of air pollutants in North America. Emission inventories of such pollutants for Canada and the United States are required in order to assess the impact of atmospheric loading using models and other techniques.

An important component of the emission of nitrogenous compounds into the atmosphere is the contribution from natural sources. These include: microorganism decomposition in soils, emissions from forest and brush fires, animal wastes, aquatic sources, and production from lightning. The primary objective of the present report, one in a series of reports dealing with natural emissions of gaseous compounds, is to provide an evaluation and quantification of nitrogenous emissions into the atmosphere in Canada. The data so derived are presented on a nationwide basis for each province.

The provision of flux estimates for various nitrogenous gases is only one objective of the study. Equally important is the provision of a framework within which new data can be incorporated. To this end, data are presented on the basis of well defined and widely recognized source units. Included in these are soil orders, and terrestrial and aquatic biome units. Data and discussions relating to ambient clean air atmospheric concentrations of the more important nitrogen compounds are also provided, as are discussions of residence times and atmospheric fates.

Data available for developing a nationwide inventory of emissions of nitrogenous compounds into the atmosphere are in most instances fragmentary. A further purpose of the present report is to identify areas where data are weak or entirely lacking. This approach allows for the development of future research priorities.

For comparative purposes, all data on fluxes have been converted to grams of nitrogen per square metre per year ($\text{g N/m}^2/\text{yr}$). In each case, the compound under consideration is identified using the notation X-N, where X denotes the compound and N signifies that measurements refer only to the nitrogen component of the compound. A list of units used to express data, together with abbreviations and, where necessary, explanations, is provided in the glossary.

2 DATA GAPS AND UNCERTAINTIES

The development of analytical procedures and methodologies necessary for detailed atmospheric studies have only recently become available. Moreover, interest in the sources and sinks of many atmospheric nitrogenous gases has only come about because of relatively recent atmospheric pollution problems. Photochemical smog and acidic precipitation have been particularly important in this regard. Consequently, the study of atmospheric chemistry, especially quantitative aspects, is still in its infancy. Considerable speculation exists in the literature as numerous authors have attempted to define global budgets of various gases from a meagre and fragmentary data base. Many studies have been undertaken in laboratories to assess the effects of various parameters on gas emission rates, but comparatively few field data are available. This is in part the result of technological problems and also because the contribution of many gases from natural sources to pollution problems has only recently become appreciated.

With respect to emissions of nitrogenous gases, the "state of the art" is in many ways at a higher level of development than that relating to other gases. This is due primarily to the long-recognized importance of nitrogen cycling to agriculture. Concern over losses of soil nitrogen and the optimum utilization of fertilizers has been the impetus for many such studies. Unfortunately, until very recently most such studies have dealt with rates of nitrate and ammonium loss without paying much attention to either the quantities of nitrogen removed by different processes or the form in which these compounds are removed. The problem is compounded by the fact that nitrogen losses from non-agricultural soils have been almost totally ignored.

For many nitrogen gases, a complete inventory of all major emission sources is lacking, let alone the availability of quantitative flux estimates. Also, where data do exist there is often considerable controversy over flux magnitudes from various sources. For example, early studies by Junge (1958), Georgii (1963) and Robinson and Robbins (1970) regarded lightning as being relatively unimportant to the production of NO_x . More recent studies by Noxon (1976, 1978), Griffing (1977), Dawson (1980), and Hill et al. (1980), despite estimates of NO_x production differing by as much as an order of magnitude, have concluded that lightning is important to NO_x production. Moreover, at least one such study concluded that lightning could be responsible for the production of as much as half of the total atmospheric NO_x (Chameides et al. 1977).

Direct emission measurements are often difficult or impossible to obtain. Hence, emission estimates have been derived through the application of various models and experimental set-ups designed to simulate natural conditions. Nitrogen gas emissions from lightning and forest and brush fires are prime examples. Varying assumptions employed in the use of such models can result in substantial differences in emission estimates. Models have also been employed to estimate fluxes where data are poor or unavailable, but where parameters governing emissions, determined through laboratory studies, are reasonably well understood. Dawson (1977), for example, developed a model to estimate NH_3 flux from different soil types based on readily available soil and biotic parameters. Unfortunately, data reported in the literature are insufficient to adequately test his model.

In extreme cases, controversy has arisen as to whether a particular unit is acting as a source or a sink for a certain gas or compound. A case in point is the movement of N_2O in relation to marine waters. Most recent studies consider marine waters to be a substantial source of N_2O (Hahn 1974, Liss and Slater 1974, Cohen and Gordon 1979, Singh *et al.* 1979). But, McElroy *et al.* (1976) regarded the ocean as a net sink for N_2O . Again, differences in results are due to differing assumptions used in the application of models designed to estimate fluxes from indirect measurements.

The present study attempts to estimate fluxes of the more important nitrogenous gases from soils, forest and brush fires, animal wastes, aquatic biomes, lightning and other sources. In most instances, good data upon which to base such estimates are not available, and in other instances, where results differ, it is not always a simple matter to assess the merits of each researcher's approach. This state of affairs has necessitated the employment of a considerable number of assumptions and extrapolations of the available data, in order to fulfill the objectives of the study. Nevertheless, it is felt that the flux estimates provided herein are useful to the task at hand and that they provide, so far as is deemed possible, the best estimates that can currently be derived. As with most such studies, flux estimates should be interpreted as order of magnitude approximations, with few exceptions.

3 MAJOR CLASSES OF NATURALLY OCCURRING ATMOSPHERIC NITROGEN COMPOUNDS - GENERAL CHARACTERISTICS

3.1 Nitrogen Oxides (NO_x)

Seven nitrogen oxides are known to be present in the ambient air, including: nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). Of these, only the first three normally occur at detectable concentrations. N_2O_5 , although present in very low concentrations, appears to be of some significance because it is an intermediate reaction product in one of the nitric acid formation series.

Despite compositional similarities between NO , NO_2 and N_2O , they behave very differently. N_2O is, with certain exceptions, largely non-reactive in the troposphere. Consequently, atmospheric concentrations of N_2O have attained comparatively high levels. NO and NO_2 , together, have fluxes comparable to that of N_2O , but because of greater reactivity potentials (Table 1), atmospheric concentrations are low. While showing certain similarities, NO and NO_2 differ in several respects, among the more important of which are thermodynamic properties and solubility. NO_2 , though not soluble per se, reacts quickly in combination with ozone, water and other reactants to produce nitric acid which is then removed from the atmosphere by precipitative and particulate scavenging. This is the major pathway by which nitrogen oxides are removed from the atmosphere. NO , on the other hand, is not appreciably soluble in water, nor does it take part in the above reactions, until first being oxidized to NO_2 .

Over the normal range of temperatures experienced at the earth's surface, NO_2 exists in equilibrium with N_2O_4 according to the reaction:



In solid state, the mixture is composed entirely of N_2O_4 . The liquid state contains trace amounts of NO_2 , normally less than 0.1%. At the boiling point (21.2°C), N_2O_4 begins to dissociate such that 16.1% of the mixture is in the form of NO_2 , and at 100°C , the gas mixture is 90% dissociated to NO_2 .

Sources of nitrogen oxides include soil microbial processes, non-biological chemical reactions in soil, forest and brush fires, ocean waters, lightning, volcanos, and possibly vegetation (Table 2). Soils and oceans constitute the largest emission source for N_2O . NO_2 and NO are emitted primarily by soils and lightning.

TABLE I SELECTED PHYSICAL AND CHEMICAL PROPERTIES OF THE MORE IMPORTANT NITROGEN COMPOUNDS LIBERATED INTO THE ATMOSPHERE FROM NATURAL SOURCES

Class and Compound	Molecular Formula	Molecular Weight	Melting Point (°C)	Boiling Point (°C)	Solubility		Rates of Reaction ((k)**)				
					Water	Ether	HO•	HO ₂	O	O ₃	
Inorganic Compounds											
Ammonia	NH ₃	17.03	- 77.7	- 33.4	soluble	soluble	1.6 x 10 ⁻¹³	-	-	-	-
Nitric oxide	NO	30.01	-163.6	-151.8	s.soluble	-	6.1 x 10 ⁻¹²	8.1 x 10 ⁻¹²	2.8 x 10 ⁻¹²	1.6 x 10 ⁻¹⁴	
Nitrogen dioxide	NO ₂	46.01	- 11.2	+ 21.2	*	-	1.6 x 10 ⁻¹¹	2.5 x 10 ⁻¹²	9.1 x 10 ⁻¹²	3.2 x 10 ⁻¹⁷	
Nitrous oxide	N ₂ O	44.01	- 90.8	- 88.5	s.soluble	soluble	<4 x 10 ⁻¹⁶	-	-	-	-
Nitriles											
Hydrogen cyanide	HCN	27.04	- 13.24	25.7	miscible	miscible	2.0 x 10 ⁻¹⁵	-	1.1 x 10 ⁻¹⁷	-	-
Amines											
Methylamine	CH ₃ NH ₂	31.06	- 93.5	- 6.3	v.soluble	miscible	2.2 x 10 ⁻¹¹	-	-	-	-
Dimethylamine	(CH ₃) ₂ NH	45.09	- 93.0	7.4	v.soluble	soluble	6.5 x 10 ⁻¹¹	-	-	-	-
Ethylamine	CH ₃ CH ₂ NH ₂	45.09	- 81.0	16.6	miscible	miscible	2.8 x 10 ⁻¹¹	-	-	-	-
n-Propylamine	CH ₃ (CH ₂) ₂ NH ₂	59.11	- 83.0	47.8	soluble	v.soluble	-	-	-	-	-

* - reacts quickly with water, but not considered soluble

** - rate constants (k) are given in cm³-molecule-sec units for gas phase reactions at 25°C, based on average tropospheric diurnal concentrations for reactants (after Graedel 1978)

- comparative k values for methane are: HO• (7.5 x 10⁻¹⁵); O (1.7 x 10⁻¹⁷); O₃ (1.4 x 10⁻²⁴)

s. soluble - slightly soluble

v. soluble - very soluble

TABLE 2 NITROGEN COMPOUNDS LIBERATED INTO THE ATMOSPHERE FROM NATURAL SOURCES (Graedel 1978)

	Sources*									
	1	2	3	4	5	6	7	8	9	10
Inorganic Nitrogen Compounds										
Nitrogen N_2								x	x	x
Ammonia NH_3	x	x	x					x	x	
Nitric oxide NO	x									x
Nitrogen dioxide NO_2	x					x		x		x
Nitrous oxide N_2O	x	x				x	x			x
Nitriles										
Hydrogen cyanide HCN	x	x								
Benzyl cyanide C_6H_5CHCN		x								
Amines										
Methylamine CH_3NH_2			x							
Dimethylamine $(CH_3)_2NH$			x							
Trimethylamine $(CH_3)_3N$	x		x							
Ethylamine $CH_3CH_2NH_2$			x							
Triethylamine $(CH_3CH_2)_3N$			x							
n-Propylamine $CH_3CH_2CH_2NH_2$			x							
Isopropylamine $(CH_3)_2CHNH_2$			x							
n-Butylamine $(CH_3)(CH_2)_3NH_2$			x							
sec-Butylamine $CH_3CH_2CH(CH_3)NH_2$			x							
Pentylamine $CH_3(CH_2)_4NH_2$			x							
Veritol $C_6H_4(OH)NHCH$		x								
Dimethylantranilate $C_6H_4NH_2$ $C(CH_3)OOCH_3$		x								
Ethylantranilate $C_6H_4NH_2$ $COOCH_2CH_3$		x								
Heterocyclic Nitrogen Compounds										
Piperine $C_{17}H_{19}NO_3$		x								
Indole $C_6H_4NHCHCH$		x	x							
Skatole $C_6H_4C_2H(CH_3)NH$			x							

* 1 - microbes; 2 - vegetation; 3 - animal wastes; 4 - insects; 5 - forest fires; 6 - oceans; 7 - volcanos; 8 - geothermal steam; 9 - natural gas; 10 - lightning

3.2 Ammonia

Ammonia occurs as a gas (NH_3), and in ionic form (NH_4^+) either in solution or as a particulate, most commonly as ammonium nitrate (NH_4NO_3) or ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). Atmospheric concentrations of NH_3 vary depending on the proximity to major sources and on ambient environmental scavenging potentials. Concentrations of from 0.50 to 15 $\mu\text{g NH}_3\text{-N/m}^3$ are typical, but in areas heavily populated by livestock, concentrations up to 70 $\mu\text{g NH}_3\text{-N/m}^3$ have been reported (Luebs et al. 1973). NH_3 flux is land-based, with the result that atmospheric concentrations over terrestrial environments are significantly greater than those observed over oceans. Ammonium is an important aerosol component, but appears to account for only a small percentage of atmospheric NH_3 .

Like other inorganic nitrogen gases, NH_3 is volatilized into the atmosphere at relatively low temperatures (Table 1), where it either reacts with oxidants or is removed by precipitative or particulate scavenging. Among the more important atmospheric reactions are oxidation by the hydroxyl radical ($\text{HO}\cdot$) and reaction with nitric acid (HNO_3). Washout or rainout is the most important atmospheric sink, removing either dissolved NH_3 or dissolved NH_4^+ compounds.

Animal wastes and soil microorganisms are the dominant emission sources. Other sources include volcanos, geothermal steam, and vegetation (Table 2). But, in the latter case it has been shown that under normal conditions, vegetation acts as a net sink for atmospheric NH_3 (Denmead et al. 1976).

3.3 Nitriles

Only two nitriles, hydrogen cyanide and benzyl cyanide, are emitted from natural sources (Table 2). Very little data relating to atmospheric parameters are available for either compound (Graedel 1978). Moreover, the extremely long lifetime of hydrogen cyanide, estimated at 38 years and reflected in its slow rate of reaction with $\text{HO}\cdot$ (Table 1), coupled with low probable atmospheric concentrations, and a high boiling point, strongly suggests that nitriles are unimportant to atmospheric chemistry. No further treatment is given to them in this report.

3.4 Amines

Although not the most important naturally emitted nitrogenous compounds, amines are certainly the most numerous (Table 2). Methyl, dimethyl and ethyl amines appear to be the most abundant such compounds in the ambient air (Mosier et al. 1973), but few data are available. Animal wastes are the predominant emission source, with

some compounds also being liberated by vegetation and, in one instance, by microbes (Table 2).

Factors of importance to ambient air amine concentrations include moderately high boiling points, high solubility in water, and high reaction potentials with hydroxyl radicals and probably other oxidants (Table 1). Reaction sequences of amines with oxidants have not been conclusively determined, but it is likely that they follow sequences similar to those experienced by atmospheric hydrocarbons (Graedel 1978). Precipitation washout appears to be the ultimate amine sink.

3.5 Heterocyclic Nitrogen Compounds

Only three heterocyclic nitrogen compounds are known to be emitted into the atmosphere by natural sources: piperine, indole and skatole (Table 2). No quantitative information is available as to either emission rates or ambient concentrations for any of these compounds. However, available evidence suggests that heterocyclic nitrogen compounds occur only in aerosol phase and at extremely low concentrations (Graedel 1978). Gas phase reactions are consequently unimportant. No further treatment is given to heterocyclic nitrogen compounds in this text.

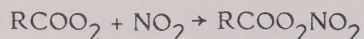
3.6 Particulate Nitrogen Compounds

Innumerable nitrogenous particulates are present in the ambient air including partially decomposed organic fragments, nitrogenous soot particulates (Chang and Novakov 1975), pollen grains, bacteria, fungal spores, salts and a host of other forms. But, from the perspective of this report only aerosols of the more important naturally emitted nitrogenous gases are considered to warrant further discussion. Of these, nitrates and ammonium compounds are the most important.

Nitric acid (HNO_3), formed by the interactions of NO_2 with either $\text{HO}\cdot$ and M (catalyst) or with O_3 and water, readily combines in the gas phase with NH_3 yielding ammonium nitrate (NH_4NO_3). Critical pressures required for this reaction of 0.4 ppb are well within ambient air concentration limits (Bottenheim and Strausz 1977). The dissociation of nitrogenous gases in vapour phase water droplets results in further aerosol production. NO_2 , NO_3 and N_2O_5 are readily soluble and/or react readily with water to produce nitrate ions (NO_3^-). These ions combine with ammonium ions (NH_4^+) to yield NH_4NO_3 , and NH_4^+ and sulphate ions (SO_4^{2-}) readily combine in vapour phase solution to form ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$.

Other nitrogen-sulphur aerosols formed in moist air environments include HNSO_5 , NOHSO_4 , NOHS_2O_7 , $\text{S}_2\text{O}_7(\text{NO})_2$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Bottenheim and Strausz 1977, Farlow et al. 1978).

Also of critical importance to nitrogen-aerosol chemistry are peroxyacetyl nitrates (PAN) formed by photochemical interactions of nitrogen oxides and hydrocarbons. The following is the most important such reaction:



Atmospheric aerosols are removed, for the most part, by wet and dry deposition mechanisms. The relative importance of these two processes in any given area is dependent upon climate and the types of aerosols present.

4 NITROUS OXIDE

4.1 Emission Sources and Flux Estimates

Nitrous oxide (N_2O) is emitted into the atmosphere from several sources including soils, oceans, fresh waters, fires, lightning and vegetation (Table 2). It is generally conceded that fluxes from soils and marine waters are the dominant global sources of N_2O (Soderlund and Svensson 1976, Cothorn 1979). Production from other sources, particularly lightning, is considerably smaller.

The principal agent of N_2O flux from soils is denitrification, during which NO_3^- is successively reduced under anaerobic conditions to NO_2 , N_2O and/or NO , and finally to N_2 . Most of the N_2O produced by this process is liberated into the atmosphere. Until recently it was generally believed that N_2O flux from oceans also arose primarily from denitrification. This belief has recently been challenged by Cohen and Gordon (1978), and others. These authors postulate that instead of producing N_2O , denitrification in seawater consumes N_2O , and that nitrification is the primary source of N_2O from marine environments. There is also some evidence that nitrification may be important to the production of N_2O from soils (Bremner and Blackmer 1978, Denmead *et al.* 1979a).

4.1.1 Terrestrial Biogenic Zones - Soils. Of the nitrogen oxides emitted into the atmosphere from natural sources, N_2O has been the most widely studied. Despite this attention, comparatively few estimates of N_2O flux from soils under natural or quasi-natural conditions are available. Considerably more emphasis has been placed on laboratory studies designed to assess factors affecting N_2O evolution from soils and their relative importance. The principal objective of such studies has centered on nitrogen losses from soils, particularly agricultural soils. Concern about quantitative flux estimates of N_2O related to global budgets have been secondary. The task of estimating N_2O fluxes from major Canadian soil orders is therefore exceedingly difficult.

The most important factors related to N_2O flux from soils are temperature, moisture content (with its resulting effects on oxygen availability), organic carbon content, and pH (Table 3). The influence of temperature on biological processes is well known. Studies specific to the task at hand have been carried out by Stanford *et al.* (1975) and Nyhan (1976). Q_{10} values, the rate of increase or decrease in biological activity for a 10°C change in temperature, derived from the works of these authors are shown in Figure 1. Their values agree well for temperatures greater than 15°C , but for lower

TABLE 3 GENERALIZED DESCRIPTIVE CHARACTERISTICS OF THE UPPERMOST 15 CM OF MAJOR CANADIAN SOIL ORDERS

Soil Order	pH	Nitrogen Content %	Organic - C Content %	Cation Exchange Capacity meq/100 g	Moisture Class	Mean Ambient Air Temperature (>0°C)							Size Distribution of Mineral Particles		
						A	M	J	J	A	S	O	Sand %	Silt %	Clay %
Chernozemic	7.1	0.30	6.47	25.5	subarid - subhumid	4	10	15	18	18	11	6	42.7	33.1	24.2
Solonchic	5.6	0.35	4.34	30.3	subarid - subhumid	4	8	12	15	13	9	3	19.7	43.2	37.2
Luvic	5.7	0.05	1.58	10.9	semiarid - humid	1	9	13	17	15	10	4	38.5	48.5	13.1
Podzolic	3.8	0.04	7.33	4.7	humid - perhumid		7	14	17	16	11	4	56.5	35.1	8.5
Brunisolic	5.3	0.09	1.66	17.2	subhumid - perhumid		6	12	14	13	8		24.6	41.8	33.5
Regosolic	6.8	0.19	<1	29.2	humid			3	9	8	2		33.0	32.7	34.3
Gleysolic	6.9	0.18	1.52	28.7	humid - subaquic		6	14	16	14	8	1	2.1	25.0	73.0
Organic	4.8	1.70	54.4	118.5	subaquic - aquatic		6	12	16	13	8	2	0.0	0.0	0.0
Rockland	-	-	<1	-	humid			5	9	8	4		-	-	-

A, M, J, J, A, S, O - months, April to October inclusive

Data from Clayton et al. (1977)

A further description of soil types is provided in Section 6.1.1.

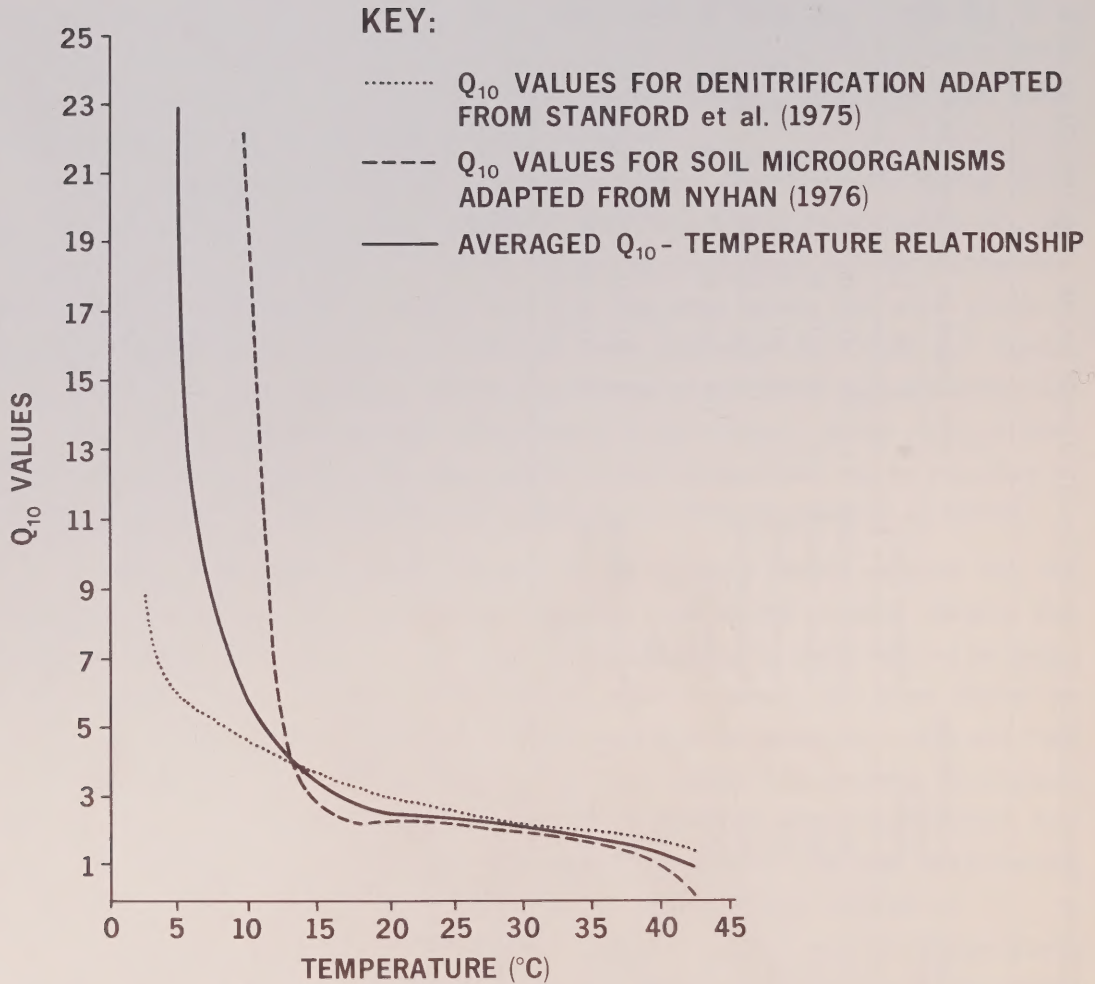


FIGURE 1 EFFECTS OF TEMPERATURE ON SOIL MICROORGANISM ACTIVITY

temperatures, differences are considerable. Given such differences, an average of the two curves has been adopted.

The effects of organic carbon content on soil denitrification appear relatively clear based on the work of Burford and Bremner (1975). They observed a direct linear relationship between increased soil organic content and increased rates of denitrification.

The effects of moisture on denitrification are considerably more complex and have not been well studied. The concern is that while anaerobic conditions are necessary for denitrification, aerobic conditions are necessary for nitrification. Without nitrification, there is no NO_3^- to feed the denitrification process. Several studies have shown that the available NO_3^- is quickly depleted under totally anaerobic conditions with the result that N_2O production falls off abruptly (Denmead et al. 1979b). The largest sustained N_2O fluxes are therefore likely to occur from soils subject to alternating periods of wetness and dryness.

The effects of pH on N_2O flux from soils are difficult to assess. Bollag et al. (1973) and Focht (1974) found that N_2O flux increased with increasing soil pH. Van Cleemput et al. (1976), Bremner and Blackmer (1978), and Bartlett et al. (1979), on the other hand, found that N_2O flux tended to increase with decreasing pH. The situation is obviously complex, and until resolved the effects of pH cannot be taken into account in a national emissions study of the present type. The effects of pH are further complicated by their influence on the ratio of $\text{N}_2\text{O} : \text{N}_2$ produced during denitrification (Focht 1974).

The following estimates of N_2O flux from soils under natural or quasi-natural conditions are available from the literature ($\text{g N}_2\text{O} - \text{N/m}^2/\text{mo}$):

Albrecht <u>et al.</u> (1970)	15.20×10^{-3}
Hahn (1974)	8.33×10^{-3}
Paul and Victoria (1976)	1.06×10^{-3}
Cothern (1979)	56.86×10^{-3}
Denmead <u>et al.</u> (1979a)	47.12×10^{-3}
Roy (1979)	23.36×10^{-3}
Mean of all sources	25.3×10^{-3}

In the absence of better information, it is assumed for purposes of this study that this average flux represents the flux from soils exhibiting average moisture conditions (humid), average organic content (3%), and a temperature of 15°C . The net effect of moisture conditions on N_2O production can best be dealt with by assuming that

optimal production occurs under humid conditions and that N_2O flux decreases to near zero under conditions of extreme dryness or extreme wetness (Denmead *et al.* 1979b). Data presented by Stefanson (1972) indicate that for a two-fold change in soil moisture content, there is an approximate 4.5-fold change in N_2O flux. The above relationships are shown in Figure 2 and are used to derive correction values for each Canadian soil type. These correction values are then applied to the generalized flux of $25.3 \times 10^{-3} \text{ g } N_2O\text{-N/m}^2\text{/mo}$ to derive standardized fluxes for each soil order (Table 4). Corrections to account for varying levels of soil organic content, derived from the equation $Y = 50.0X + 6.2$ from Burford and Bremner (1975), where Y equals the rate of denitrification and X equals soil organic content, are also shown in Table 4.

TABLE 4 ESTIMATED MONTHLY FLUXES OF N_2O FROM CANADIAN SOIL ORDERS STANDARDIZED TO 15°C^*

Soil Order	Estimated Conversion Factors		Estimated Flux at 15°C ($\text{g } N_2O\text{-N/m}^2\text{/mo}$)
	Moisture	Organic Content	
Chernozemic	0.35	2.1	18.6×10^{-3}
Solonetzic	0.35	1.4	12.4×10^{-3}
Luvisolic	0.45	0.54	6.1×10^{-3}
Podzolic	0.80	2.4	48.6×10^{-3}
Brunisolic	1.00	0.57	14.4×10^{-3}
Regosolic	1.00	0.25	6.8×10^{-3}
Gleysolic	0.55	0.53	7.4×10^{-3}
Organic	0.10	17.5	44.3×10^{-3}
Rockland	-	-	-

* Data assume a global soil flux of $25.3 \times 10^{-3} \text{ g } N_2O\text{-N/m}^2\text{/mo}$ for soils with an organic carbon content of 3% and humid moisture conditions.

Estimated monthly N_2O fluxes per square metre are determined in the following manner. Consider, for example, that in the month of May the average temperature for chernozemic soils is about 10°C . From Figure 1 the Q_{10} value between this temperature and our 15°C standard is approximately 4.3. Consequently, a 10°C

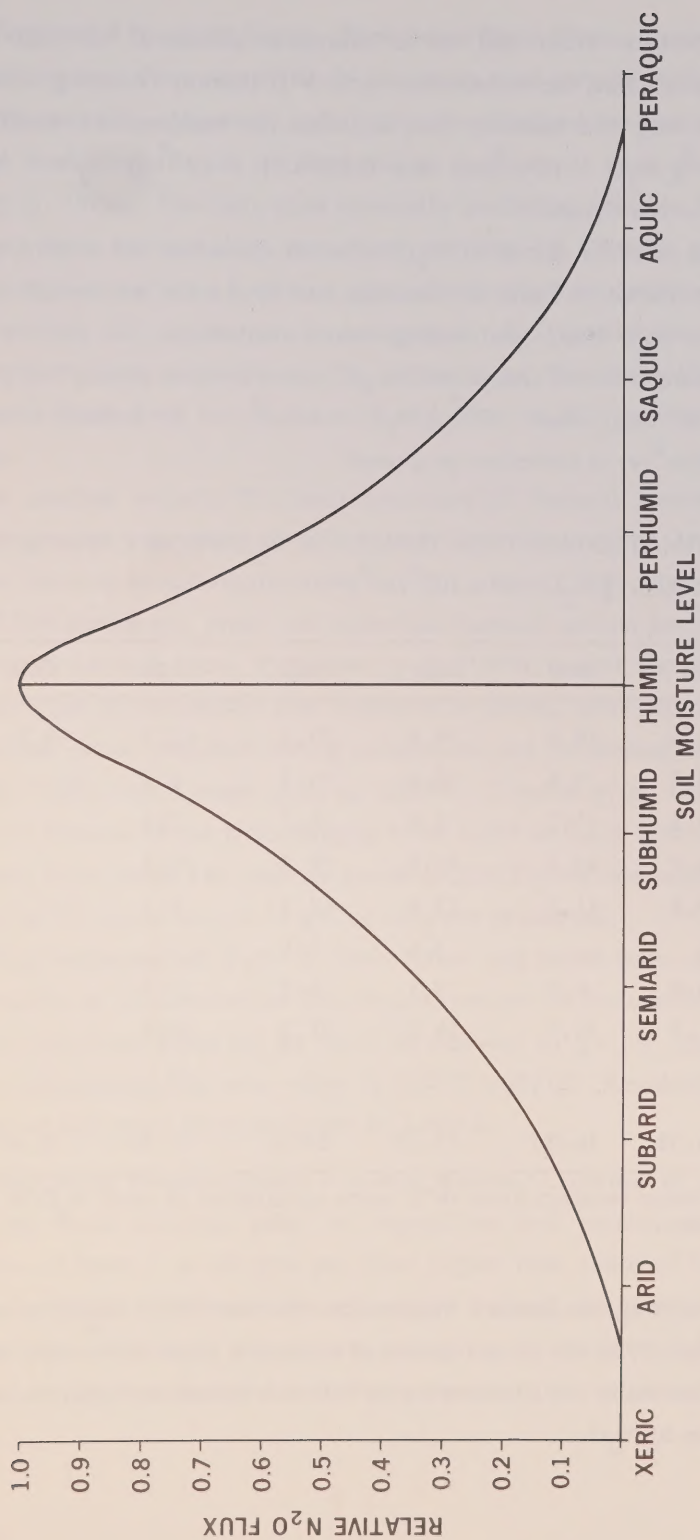


FIGURE 2 RELATIONSHIP BETWEEN N_2O FLUX FROM SOILS AND SOIL MOISTURE CONTENT

reduction in temperature from the 15°C standard yields a 4.3-fold decrease in microbiological activity. But, the reduction is only 5°C thereby resulting in only half this change. Hence, for May the monthly flux adjusted for temperature would be midway between $18.6 \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{mo}$ and $(18.6/4.3) \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{mo}$, or $11.5 \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{mo}$.

Estimated monthly fluxes of N_2O from all Canadian soil orders, based on the above procedure, are shown in Table 5. Data on rockland soils are insufficient to allow calculation of annual N_2O flux. But taking into consideration the shallow soil, sparse vegetation and low temperatures characteristic of most rockland areas, it is probable that the annual flux is less than $10^{-2} \text{ g N}_2\text{O} - \text{N/m}^2$. A tentative estimate of $5 \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$ is therefore proposed.

TABLE 5 ESTIMATED MONTHLY FLUXES OF N_2O FROM CANADIAN SOIL ORDERS ($\text{g N}_2\text{O} - \text{N} \times 10^{-3}/\text{m}^2$)*

Soil Order	May	June	July	Aug.	Sept.	Oct.	Annual
Chernozemic	11.5	18.6	29.8	29.8	12.9	4.8	107.4
Solonetzic	5.7	9.6	12.4	10.5	6.7	-	44.9
Luvisolic	3.3	5.2	8.8	6.1	3.8	-	27.2
Podzolic	16.7	45.1	70.0	59.8	33.8	-	225.4
Brunisolic	3.8	11.1	13.4	12.2	6.5	-	47.0
Regosolic	-	-	3.6	3.1	-	-	6.7
Gleysolic	0.1	6.9	9.1	6.9	3.3	-	26.3
Organic	11.5	34.3	54.5	37.7	19.9	-	157.9
Rockland	-	-	-	-	-	-	-
Mean Values	6.58	16.35	25.20	20.76	10.86	0.60	80.35

* Only months with mean temperatures $\geq 4^\circ\text{C}$ were considered to emit N_2O in appreciable quantities.

4.1.2 Terrestrial Biogenic Zones - Vegetation. Nitrous oxide (N_2O) is known to be a plant volatile (Graedel 1978), but no estimates of emissions from this source are available, nor is there any indication in the literature that this source has any relative importance to overall emission rates of N_2O .

4.1.3 Terrestrial Biogenic Zones - Forest and Brush Fires. Emissions data on gases evolved during natural fires are difficult to obtain, and consequently there are few such measurements available. Moreover, what data are obtained are frequently highly variable depending on characteristics of the fire and on methods of data collection and analysis (Fritschen *et al.* 1970). The only data currently available, suitable for the estimation of NO_x emissions from natural fires, are those provided by Crutzen *et al.* (1979). These authors measured quantities of various gases produced from forest fires on the basis of volume ratios using CO_2 production as a standard. N_2O production was estimated on a volume per volume basis at 0.22% of CO_2 production. Therefore flux estimates of N_2O from forest and brush fires can be made if estimates of CO_2 production from such fires are available.

In another report, "National Inventory of Natural Sources and Emissions of Organic Compounds" estimates of CO fluxes from the major Canadian biomes were provided (The Environmental Applications Group Limited 1980). These data were based on estimates of fire frequency, areas and materials burned, and on emission estimates from natural and quasi-natural fires. Fritschen *et al.* (1970), one of the principal sources used in the computation of emission rates referred to above, provided several estimates of CO/ CO_2 volume ratios obtained during prescribed and controlled burns. Values ranged from 0.000 to 0.200 with a mean ratio of 0.0577. Crutzen *et al.* (1979) provided similar estimates from natural forest fires ranging from 0.055 to 0.216 with a mean ratio of 0.14. Averaging data from these two sources yields a CO/ CO_2 volume ratio of 0.0989. Hence, for every g C of CO produced, 10.11 g C of CO_2 are produced.

Flux estimates of N_2O - N from forest and brush fires can be determined by multiplying values of CO production (National Inventory of Natural Sources and Emissions of Organic Compounds, Table 28) by 10.11 to convert to g C of CO_2 produced, and by subsequently multiplying this new value by $0.0022 \times 28/12$. Resulting flux estimates for N_2O from forest and brush fires are given in Table 6.

4.1.4 Terrestrial Biogenic Zones - Animal Wastes. Cicerone *et al.* (1978) found that gases evolving from compost piles of vegetation and animal manure showed N_2O concentrations of from 1 to 20 ppm per hour higher than those of background measurements. Unfortunately, a determination of relative proportions of plant and animal matter was not provided. Moreover, the process giving rise to these emissions was most likely denitrification, a process already taken into account in the estimates of N_2O production

TABLE 6 ESTIMATES OF N_2O FLUX FROM FOREST AND BRUSH FIRES ($g N_2O - N \times 10^{-3}/m^2/yr$)

Biome	Maritimes	Prairies-Territories	British Columbia
Tundra	-	-	-
Boreal Forest - Barrens	0.265	0.487	-
Boreal Forest	1.053	1.955	-
Aspen Parkland	-	0.975	-
Coastal and Mountain Forests	-	-	0.487
Great Lakes - Acadian Forests	1.261	-	-
Grassland - Agriculture	0.019	0.019	0.019

from soils. Consequently, there is no indication that animal wastes in themselves are an important source of N_2O .

4.1.5 Aquatic Biogenic Zones - Freshwater. The only estimate of N_2O flux from fresh waters is that provided by Cothern (1979) of $(1.3 \text{ to } 3.2) \times 10^{-8} g N_2O - N/m^2/sec$. This estimate applies largely to enriched systems. Moreover, Cothern (1979) considered that significant amounts of N_2O would only be evolved from sediments at depths greater than 30 m. At these depths, temperatures of Canadian lakes appear rarely to exceed $7^\circ C$ (Schindler 1971). Denitrification rates at such low temperatures are extremely slow (Figure 1). It is therefore reasonable to assume the N_2O flux from relatively unpolluted Canadian lakes is negligible.

4.1.6 Aquatic Biogenic Zones - Marine Waters. McElroy *et al.* (1976) stand alone in regarding oceans as a net sink for N_2O . Their results are based on the assumption that the major source of N_2O production from marine waters is denitrification. This assumption has been refuted by Cohen and Gordon (1979). All other researchers regard oceanic areas as net sources of N_2O , and except for Arctic regions, several good flux estimates are available.

Global oceanic fluxes of N_2O are available from the literature as follows ($g N_2O - N/m^2/yr$):

Liss and Slater (1974)	0.211
Hahn and Junge (1977)	0.125 (0.004-0.443)
Cohen and Gordon (1979)	0.011 - 0.027
Cothorn (1979 citing unpubl. data from R.J. Weirs)	0.010

Hahn (1974) estimated production from the North Atlantic at about $0.171 \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$. He also found that temperature effects appeared to be negligible, with no consistent pattern. For example, surface water concentrations of N_2O , upon which his estimates were based, were $0.40 \text{ }\mu\text{g/L}$, $0.53 \text{ }\mu\text{g/L}$, and $0.46 \text{ }\mu\text{g/L}$ for $40^\circ - 50^\circ \text{ N}$, $50^\circ - 60^\circ \text{ N}$, and above 60° N , respectively. Similar observations of a relative lack of temperature influence also appear to hold for the Pacific. Singh *et al.* (1979) reported fluxes of $0.072 \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$ and $0.062 \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$ for areas of the Pacific between 45° S and 45° N , and north of 45° N , respectively. Temperature limitations on N_2O evolution from oceans appear, therefore, only to be manifested through the phenomenon of ice cover. When data are averaged, ice-free areas of the Atlantic (Hahn 1974, Hahn and Junge 1977, Cothorn 1979) appear to be similar in their N_2O production to those of the Pacific (Singh *et al.* 1979). Consequently, all ice-free ocean sections in Canadian waters are regarded as having the same flux of approximately $0.101 \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$. Data on Canadian marine ice conditions presented by Allen (1977) indicate that on average: Arctic regions are frozen for eight to nine months of the year; Pacific regions normally do not freeze over; the region referred to as Atlantic North is frozen for approximately five months; about half of the Atlantic South region is frozen for approximately four months, but the outer coasts of Newfoundland and Nova Scotia and the Bay of Fundy do not freeze.

Assuming that ice-covered marine waters do not liberate N_2O into the atmosphere, the following flux estimates for Canadian marine waters are derived ($\text{g N}_2\text{O} - \text{N/m}^2/\text{yr}$):

Arctic Regions	0.029
Pacific Regions	0.101
Atlantic Region - North	0.059
Atlantic Region - South	0.084

4.1.7 Production from Lightning. Comparatively few estimates of N_2O production from lightning are available and those that do exist differ considerably. Griffing (1977) estimated the global production of N_2O from lightning at $2.93 \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$.

Hill *et al.* (1980), on the other hand, concluded that N_2O production from lightning was not important, and Levine *et al.* (1979) estimated a global production rate of only $8.79 \times 10^{-6} \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$. While it appears that the latter estimate is the more reliable of the two in view of support from Hill *et al.* (1980), a weighted average of the above estimates (i.e., a 2:1 weighting factor favouring the latter estimate) has been used, resulting in an estimated global flux of $0.98 \times 10^{-3} \text{ g N}_2\text{O} - \text{N/m}^2/\text{yr}$.

Global lightning distributions have not been adequately determined (Prentice 1977). Fortunately, global and national maps showing thunderstorm activity are available. These allow for general comparisons suitable to the relative estimation of lightning activity. Boucher (1975 p. 39) provided data in map form of the global distribution of thunderstorms, measured in average numbers of days per year in which thunderstorms are likely to occur. A strong concentration of storm activity exists in the tropics, moderate activity in temperate zones, and almost no activity in polar regions. Dot-grid sampling of the map provided by Boucher (1975) yields a global average of approximately 32.8 thunderstorm days per year.

Data on the distribution of thunderstorm days in Canada are provided by Kendall and Petrie (1962). Average annual distributions calculated by these authors show a strong correlation with biomes used in this report. Dot-grid sampling of their data yields estimates of thunderstorm activity for each biome relative to the global average. Assuming that thunderstorm activity is positively correlated with lightning frequency it is then possible to estimate $\text{N}_2\text{O} - \text{N}$ production from lightning for Canadian biomes (Table 7).

4.2 Atmospheric Concentrations

As a result of the extremely long lifetime exhibited by N_2O , with estimates ranging from 2 to 150 years (Singh *et al.* 1979), atmospheric mixing and hence global atmospheric concentrations in clean air environments are considerably more uniform than those found for other gases. Estimates of atmospheric N_2O concentrations in the lower terrestrial troposphere range from 263 to 474 $\mu\text{g N}_2\text{O} - \text{N/m}^3$, with an estimated mean of 357.6 $\mu\text{g N}_2\text{O} - \text{N/m}^3$ (Table 8). Average N_2O concentrations from terrestrial and marine atmospheres are comparable at 354.7 and 360.5 $\mu\text{g N}_2\text{O} - \text{N/m}^3$, respectively. Estimates from land areas, however, are more variable (Table 8). Global estimates shown in Table 8, averaging 324.3 $\mu\text{g N}_2\text{O} - \text{N/m}^3$, are slightly lower than averaged observed values.

Vertical profile descriptions of N_2O atmospheric concentrations provided by Roy (1979) indicate a slightly lower concentration at an altitude of 10 to 12 km, 332 ppb

TABLE 7 ESTIMATES OF N₂O PRODUCED BY LIGHTNING*

Biome	Mean Annual Frequency of Thunderstorm Days	Estimated N ₂ O Flux (g N ₂ O - N x 10 ⁻³ /m ² /yr)
Tundra	1.7	0.051
Boreal Forest - Barrens	6.5	0.194
Boreal Forest	13.0	0.388
Aspen Parkland	20.8	0.621
Coastal and Mountain Forest	9.0	0.269
Great Lakes - Acadian Forests	18.0	0.538
Grassland - Agriculture	22.5	0.672

* Estimates assume a global average production of 0.98×10^{-3} g N₂O - N/m²/yr and an average global thunderstorm rate of 32.8 days per year.

TABLE 8 BACKGROUND ATMOSPHERIC CONCENTRATIONS OF N₂O IN CLEAN AIR (μg N₂O - N/m³)

Terrestrial	Marine	Assumed Global Averages
329-474 Massachusetts Goody (1969)	323-389 Atlantic Cohen & Gordon (1979)	293-312 Rasmussen <u>et al.</u> (1975)
263-370 Germany Schutz <u>et al.</u> (1970)	329-340 North Pacific Cohen & Gordon (1979)	308 McElroy <u>et al.</u> (1976)
284 Colorado Moore (1974)	374-412 Australia-Antarctica Roy (1979)	332-378 Liu <u>et al.</u> (1977)
380-403 Michigan Cicerone <u>et al.</u> (1978)	349-371 Southern Hemisphere Singh <u>et al.</u> (1979)	296 Knelson & Lee (1977)
352-408 Iowa Matthias <u>et al.</u> (1979)	349-369 Northern Hemisphere Singh <u>et al.</u> (1979)	349-371 Singh <u>et al.</u> (1979)

(107.2 $\mu\text{g N}_2\text{O} - \text{N/m}^3$), as compared with 337 ppb (399.3 $\mu\text{g N}_2\text{O} - \text{N/m}^3$) in the lower troposphere. Seasonal variations in atmospheric concentrations were reported by Goody (1969) who found concentrations were highest in the spring. No explanation for this phenomenon could be found. Daily variations in N_2O atmospheric concentrations close to ground level ranging from 361 to 409 $\mu\text{g N}_2\text{O} - \text{N/m}^3$ have also been reported (Matthias *et al.* 1979).

However, compared with measurements reported for other gases, N_2O exhibits relatively constant values with respect to time of day, and season.

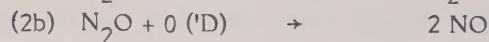
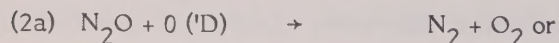
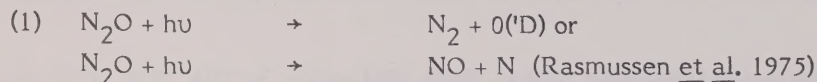
4.3 Residence Times and Atmospheric Fates

4.3.1 Residence Times. A variety of models have been employed to estimate the atmospheric lifetime of N_2O based on atmospheric concentration, vertical mass movements and stratospheric destruction rates. Given that many of these parameters are as yet not completely understood, it is not surprising that lifetime estimates vary widely, ranging from 4 to 200 years (Table 9). Except for estimates by Jung (1974), Hahn (1974) and Junge and Hahn (1971), most values including the more recent ones are in the order of 100 years. But all estimates involve considerable speculation (Soderlund and Svensson 1976).

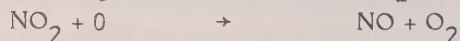
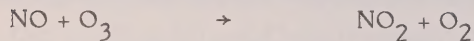
TABLE 9 ESTIMATED LIFETIMES OF N_2O

Estimated Lifetimes (years)	Source
70	Bates and Hays (1967)
70	Schutz <i>et al.</i> (1970)
5 - 15	Junge and Hahn (1971)
12 - 13	Hahn (1974)
4 - 16	Junge (1974)
170	Johnston and Selwyn (1975)
< 200	Soderlund and Svensson (1976)
30 -100	Liu <i>et al.</i> (1977)
75 -110	Singh <i>et al.</i> (1979)

4.3.2 Atmospheric Fates. Despite uncertainties, the long lifetime of N_2O suggests that it is comparatively unreactive. Only two N_2O sinks, both in the stratosphere, have been demonstrated to be of importance. These include (1) photolysis and (2) reaction series initiated by an excited state oxygen (Rasmussen et al. 1975, McElroy et al. 1976, Pierotti and Rasmussen 1976, Liu et al. 1977, Cicerone et al. 1978, and Cothern 1979).



with subsequent reactions



Reactions 2a and 2b proceed at approximately the same rate, each accounting for the removal of about 1.0 Tg of N_2O annually (Cothern 1979). Reaction series 2b is the major source of stratospheric nitrogen oxides (Cicerone et al. 1978, Cothern 1979). Photolysis, however, is the major proven sink for N_2O , accounting for the removal of from 20 to 40 Tg annually.

Other suggested N_2O sinks include absorption by soils and vegetation (Rasmussen et al. 1975, Blackmer and Bremner 1976, Freney et al. 1978) and reactions with $HO\cdot$ and $HO_2\cdot$ (Cothern 1979). None of these pathways appears to be of any significance. One N_2O removal mechanism showing potential, but which is as yet unproven, involves high-temperature, thermal-photochemical decomposition of sand-absorbed N_2O (Cothern 1979). Theoretically, this mechanism has the potential to remove as much as 70 Tg of N_2O annually (Cothern 1979). Data documenting such a removal rate are lacking. However, if this estimate should prove realistic, atmospheric lifetimes of N_2O would be considerably shorter than presently accepted values.

5 NITRIC OXIDE AND NITROGEN DIOXIDE

5.1 Emission Sources and Flux Estimates

Known natural emission sources of NO_x include soils, forest and brush fires, lightning, and possibly marine waters (Table 2), with soils and lightning being the most important.

5.1.1 Terrestrial Biogenic Zones - Soils. Estimates of NO_x flux from soils amended with various nitrogen compounds, under laboratory conditions, are available from a limited number of sources (Ratsch and Tingey 1977), but only two sources provide estimates of NO_x flux from soils measured under natural or quasi-natural conditions. Makarov (1969, cited by Soderlund and Svensson 1976) reported values of $(0.3 - 7) \times 10^{-9}$ g NO_x - N/m²/s. Similar estimates, ranging from $(5.5 - 13) \times 10^{-9}$ g NO_x - N/m²/s, were reported by Kim (1973) for soils of pH range 5.6 to 6.0 and various vegetation cover types. Because of the limited data base, extrapolations derived are tenuous. Unfortunately, no other flux estimates are available. Also, given the high boiling point of NO_2 and its association with N_2O_4 , almost all NO_x produced by soils is in the form of NO.

NO_x production from soils is dependent on three processes: nitrification, denitrification and nitrosation. During nitrification the NO_3^- necessary to the remaining processes is formed under aerobic conditions. Denitrification then results in the reduction of NO_3^- to NO_2^- which combines with H^+ to form nitrous acid (HNO_2). The HNO_2 formed subsequently undergoes non-biological chemical breakdown (nitrosation) to yield NO which is then oxidized to NO_2 . Since nitrification and denitrification are both involved, factors affecting NO_x evolution include soil moisture, organic content, temperature and pH. The first three factors behave in a manner similar to that described for N_2O flux. Consequently, a similar set of correction factors has been employed to account for the influence of these parameters on flux estimates as provided by Makarov (1969) and Kim (1973).

The effects of pH on the nitrosation process, while not fully documented, are sufficient to warrant special attention. Optimal conditions required for the liberation of NO_x from soils appear to be between pH 4 and 5 (Junge 1963, Bollag et al. 1973, Van Cleemput et al. 1976). The lower estimate provided is based on the assumption that microbial activity is reduced by excessive acidity. A mathematical relationship between NO_x production from soils and soil pH is not yet available, but in the absence of better data the relationship is assumed to be logarithmic.

Van Cleemput et al. (1976) provided data on NO flux taken from amended soils under laboratory conditions at pH 4.5, 6.0 and 8.0. NO production at pH 4.5 was approximately eleven times that produced at pH 6.0, and no NO was detected at pH 8.0.

Assuming these values lie on a line described by a simple logarithmic (natural) relationship, it is then possible to use this relationship to derive correction factors to apply to estimates provided by Makarov (1969) and Kim (1973). These are shown in Table 10.

Monthly estimates of NO_x flux from major Canadian soil groups based on procedures outlined in Section 4.1.1 are shown in Table 11. The annual flux estimate for rockland soil types is little more than an educated guess based on presumed soil availability, organic content, pH, moisture and temperatures.

5.1.2 Terrestrial Biogenic Zones - Vegetation. There is no evidence that NO_x is liberated directly by vegetation other than through decomposition of litter by soil and other microorganisms (Ratsch and Tingey 1977).

5.1.3 Terrestrial Biogenic Zones - Forest and Brush Fires. A discussion of available data and computation procedures necessary to estimate NO_x flux from forest and brush fires is provided in Section 4.1.3. Crutzen et al. (1979) estimated NO_x flux from forest fires to be 0.47% of CO_2 production on a volume-per-volume basis. Flux estimates of NO_x - N from forest and brush fires for each of the major Canadian biomes can therefore be determined by multiplying values of CO production (see Section 4.1.3) by 10.11 to convert to g C of CO_2 produced, and by subsequently multiplying this new value by $0.0047 \times 14/12$. Resulting flux estimates for NO_x from forest and brush fires are provided in Table 12.

Crutzen et al. (1979) did not attempt to separate NO_x into NO and NO_2 components. While it appears that at least some of the NO_x released is in the form of NO (Schiff et al. 1979), it would also appear that this component is negligible or nearly so when compared to NO_2 production (Radke et al. 1978). Presumably this is the result of high oxidation potentials which readily convert NO to NO_2 in the presence of ozone and other oxidants. Almost all NO_x produced is therefore in the form of NO_2 .

TABLE 10 ESTIMATED MONTHLY FLUXES OF NO_x FROM CANADIAN SOIL ORDERS STANDARDIZED TO 15°C^*

Soil Order	Moisture	Estimated Conversion Factors Organic Content	pH	Estimated Flux at 15°C ($\text{g NO}_x - \text{N/m}^2/\text{mo}$)
Chernozemic	0.35	0.76	0.1	0.45×10^{-3}
Solonchetic	0.35	0.51	1.1	3.36×10^{-3}
Luviosolic	0.45	0.19	0.9	1.32×10^{-3}
Podzolic	0.80	0.86	5.0	58.82×10^{-3}
Brunisolic	1.00	0.20	1.8	6.16×10^{-3}
Regosolic	1.00	0.09	0.2	0.31×10^{-3}
Gleysolic	0.55	0.18	0.1	0.17×10^{-3}
Organic	0.10	6.40	4.0	43.78×10^{-3}
Rockland	-	-	-	-

* Data assume a global soil flux of $17.1 \times 10^{-3} \text{ g NO}_x - \text{N/m}^2/\text{mo}$ for soils with 8.5% organic content, humid moisture conditions and a pH of 5.7.

TABLE 11 ESTIMATED MONTHLY FLUXES OF NO_x FROM CANADIAN SOIL ORDERS (g NO_x - N x 10⁻³/m²)

Soil Order	Month ¹						Annual
	May	June	July	Aug.	Sept.	Oct.	
Chernozemic	0.3	0.5	0.7	0.7	0.3	0.1	2.60
Solonetzic	1.5	2.6	3.4	2.9	1.8	-	12.20
Luvisolic	0.7	1.1	1.9	1.3	0.8	-	5.80
Podzolic	20.2	54.6	84.7	72.4	40.9	-	272.80
Brunisolic	1.6	4.7	5.7	5.2	2.8	-	20.00
Regosolic	-	-	0.2	0.2	-	-	0.40
Gleysolic	0.0	0.2	0.2	0.2	0.1	-	0.70
Organic	11.4	34.0	54.0	37.3	19.7	-	156.40
Rockland							0.30
Mean Values	4.46	12.21	18.85	15.03	8.30	0.01	58.86

¹Only months with mean temperatures $\geq 4^{\circ}\text{C}$ were considered to emit NO_x in appreciable quantities.

Note: flux from rockland areas is not included in the annual mean.

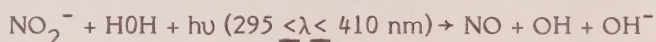
5.1.4 Terrestrial Biogenic Zones - Animal Wastes. There is no indication in the literature that NO_x could be emitted as an animal waste product.

5.1.5 Aquatic Biogenic Zones - Freshwater. Galbally (1975) concluded that mechanisms necessary for the production of NO_x in fresh waters, excluding sediments, were not known to exist. However, recent studies by Zafiriou *et al.* (1980) in marine environments suggest that such a mechanism may exist. No data are available to further the discussion.

TABLE 12 ESTIMATES OF NO_x FLUX FROM FOREST AND BRUSH FIRES
(g NO_x - N x 10⁻³/m²/yr)

Biome	Ont. - Que. - Maritimes	Prairies-Territories	British Columbia
Tundra	--	--	--
Boreal Forest - Barrens	0.283	0.520	--
Boreal Forest	1.125	2.088	--
Aspen Parkland	--	1.041	--
Coastal and Mountain Forests	--	--	0.520
Great Lakes - Acadian Forests	1.347	--	--
Grassland - Agriculture	0.020	0.020	0.020

5.1.6 Aquatic Biogenic Zones - Marine Waters. Until very recently it was thought that marine waters did not emit NO_x. Studies by Zafiriou *et al.* (1980), however, indicate that NO is produced from surface water through sunlight. Photolysis of NO₂⁻ occurs via the reaction:



The reaction has only been studied in tropical waters and no estimates of NO flux from this source are available. Moreover, there is no indication that NO is produced by this mechanism in either temperate or polar regions.

5.1.7 Production from Lightning. Earlier studies considered lightning to be unimportant in the production of nitrogen oxides, since there appeared to be no correlation between NO₃⁻ in rainwater and lightning intensity (Junge 1958, Georgii 1963, Robinson and Robbins, 1970). More recent studies, however, have indicated that this is probably not the case (Noxon 1976, 1978, Chameides *et al.* 1977, Griffing 1977, Dawson 1980, Hill *et al.* 1980).

Noxon (1976, 1978) estimated that approximately 10^{26} molecules of NO_2 were produced per lightning flash. Assuming a global lightning flash frequency of 10^2 flashes per second (Noxon 1978, Dawson 1980, Hill et al. 1980), this translates to 0.618×10^{21} molecules/ m^2/yr , or $14.4 \times 10^{-3} \text{ g NO}_x - \text{N}/\text{m}^2/\text{yr}$. Global estimates of NO_x production by lightning provided by, or derived from, data presented by other researchers are as follows ($\text{g NO}_x - \text{N}/\text{m}^2/\text{yr}$):

Chameides <u>et al.</u>	(1977)	73.2×10^{-3}
Chameides	(1979)	152.5×10^{-3}
Griffing	(1977)	58.7×10^{-3}
Dawson	(1980)	6.15×10^{-3}
Hill <u>et al.</u>	(1980)	8.62×10^{-3}

Differences in estimates are considerable, with major discrepancies resulting primarily from differing estimates of per stroke energy (Hill et al. 1980, Chameides et al. 1977, Chameides 1979). Averaging the above estimates of NO_x production from lightning yields a global average of $52.3 \times 10^{-3} \text{ g NO}_x - \text{N}/\text{m}^2/\text{yr}$. Considering statements by Dawson (1980) and considering that the majority of authors regard their estimates as generally high, the above average should be viewed as an upper limit.

The proportion of $\text{NO}-\text{N}$ to NO_2-N produced by lightning was estimated by Griffing to be approximately 37%. Chameides et al. (1977), on the other hand, considered that most NO_x initially produced was NO , but that the oxidation of NO to NO_2 via the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ was so rapid that the problem of $\text{NO} - \text{NO}_2$ proportions is academic.

Estimates of thunderstorm activity, presumably reflective of lightning activity, in each of the seven major biomes was provided in Section 4.1.7. Using these data and the global average of $52.3 \times 10^{-3} \text{ g NO}_x - \text{N}/\text{m}^2/\text{yr}$, estimates of NO_x production on a per biome basis can be derived (Table 13).

5.2 Atmospheric Concentrations

Atmospheric concentrations of NO and NO_2 are considerably more variable than those of N_2O , primarily because of comparatively short lifetimes exhibited by these compounds. As a result, atmospheric concentrations are strongly influenced by source strengths. Concentrations of NO over land areas range from 0.00 to $1.29 \mu\text{g NO} - \text{N}/\text{m}^3$ with a mean of $0.57 \mu\text{g NO} - \text{N}/\text{m}^3$ (Table 14).

TABLE 13 ESTIMATES OF NO_x PRODUCTION BY LIGHTNING*

Biome	Mean Annual Frequency of Thunderstorm Days	Estimated NO _x Flux (g NO _x - N x 10 ⁻³ /m ² /yr)
Tundra	1.7	2.72
Boreal Forest - Barrens	6.5	10.36
Boreal Forest	13.0	20.71
Aspen Parkland	20.8	33.16
Coastal and Mountain Forests	9.0	14.35
Great Lakes - Acadian Forests	18.0	28.71
Grassland - Agriculture	22.5	35.88

*Estimates assume a global average production of 52.3×10^{-3} g NO_x - N/m²/yr and an average global thunderstorm rate of 32.8 days per year

Measurements of marine atmosphere NO concentrations are available from Schiff *et al.* (1979), and from Lodge *et al.* (1974) for the American tropics. Estimates from the latter source range from 0.177 to 0.413 µg NO - N/m³ which agree reasonably well with average terrestrial air mass estimates. Global NO atmospheric concentrations average 0.87 µg NO - N/m³ (Table 14). NO₂ concentrations from terrestrial air masses range from 0.04 to 12.44 µg NO₂ - N/m³ with a mean of 1.17 µg NO₂ - N/m³ (Table 14). As might be expected given the short lifetimes of NO_x, seasonal and daily changes in atmospheric concentrations can be quite large. Ripperton *et al.* (1970), for example, found that September atmospheric NO concentrations, measured near the ground, in North Carolina varied from 0.00 to 10.7 µg NO - N/m³, but variations of from 0.00 to 2.7 µg NO - N/m³ are more typical. The primary factor affecting NO concentration appeared to be ozone levels. NO is readily oxidized to NO₂ by ozone. NO₂ also showed strong daily concentration fluctuations affected by both ozone levels and sunlight.

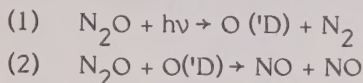
TABLE 14 BACKGROUND ATMOSPHERIC CONCENTRATIONS OF NO_x IN
CLEAN AIR ($\mu\text{g NO}_x - \text{N/m}^3$)

NO ₂ Terrestrial	Marine	Assumed Global Average
1.09 - 1.29 North Carolina Ripperton <u>et al.</u> (1970)	0.18 - 0.41 American tropics Lodge <u>et al.</u> (1974)	0.93 Robinson and Robbins (1970)
0.00 - 0.94 American tropics Lodge <u>et al.</u> (1974)	<0.02 Global Schiff <u>et al.</u> (1979)	0.93 - 1.21 Rasmussen <u>et al.</u> (1975)
0.00 - 1.20 S.W. Ireland Cox (1977)		0.59 Griffing (1977)
<0.02 - 0.04 North America Schiff <u>et al.</u> (1979)		
NO ₂		
<0.86 Florida Junge (1956)	0.39 - 1.89 Hawaii Junge (1957)	0.00 - 1.78 Junge (1963)
0.74 Hawaii Junge (1956)	<0.60 mid-Pacific Lodge <u>et al.</u> (1960)	0.30 land areas north of 65°N and south of 65°S and oceans Robinson and Robbins (1970)
0.13 - 0.19 S.W. Ireland O'Connor (1962)	<0.29 - 2.86 Caribbean Lodge and Pate (1966)	2.37 land areas 65°S - 65°N Robinson and Robbins (1970)
<0.12 - 1.18 Antarctica Fisher <u>et al.</u> (1968)	0.30 - 0.70 American tropics Lodge <u>et al.</u> (1974)	0.59 Oceanic areas Warneck (1974)
<0.29 - 2.29 Panama Lodge and Pate (1966)		1.18 - 2.37 land areas Warneck (1974)

TABLE 14 BACKGROUND ATMOSPHERIC CONCENTRATIONS OF NO_x IN
CLEAN AIR ($\mu\text{g NO}_x - \text{N/m}^3$) (Cont'd.)

NO ₂ Terrestrial	Marine	Assumed Global Average
1.94 - 4.35 North Carolina Ripperton <u>et al.</u> (1970)		0.61 - 0.79 Rasmussen <u>et al.</u> (1975)
0.59 - 1.78 Central United States Breeding <u>et al.</u> (1973)		0.59 Griffing (1977)
0.12 - 1.78 Southern Ontario Brewer <u>et al.</u> (1973)		0.12 Western Hemisphere Noxon (1978)
0.06 - 0.46 American tropics Lodge <u>et al.</u> (1974)		
0.04 - 0.17 Colorado Moore (1974)		
2.37 - 12.44 rural England Nash (1974)		
<0.06 Colorado Noxon (1976, 1978)		
0.06 - 0.86 S.W. Ireland Cox (1977)		

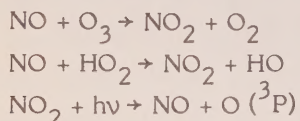
Variations in vertical concentrations of odd nitrogen compounds were discussed in detail by McConnel and McElroy (1973). These authors found that NO mixing ratios increased with altitude such that concentrations at 40 to 80 km were two orders of magnitude greater than tropospheric concentrations. This is attributable to stratospheric photolysis of both NO_2 ($\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$) and N_2O (1,2):



NO_2 mixing ratios are highest at elevations of 30 to 40 km, but decrease rapidly above 40 km because of the above photolysis reaction (McConnel and McElroy 1973). Surface concentrations are about one order of magnitude less than concentrations at an elevation of 30 to 40 km.

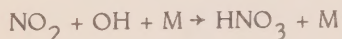
5.3 Residence Times and Atmospheric Fates

Soderlund and Svensson (1976) estimated NO_x lifetimes of from 1 to 20 days, exclusive of intergeneric photochemical reactions. Lifetime estimates inclusive of intergeneric reactions are considerably less, 1.1 minutes and 1.7 minutes for NO and NO_2 , respectively (Graedel 1978). Intergeneric NO_x reactions are dominated by the reactions:

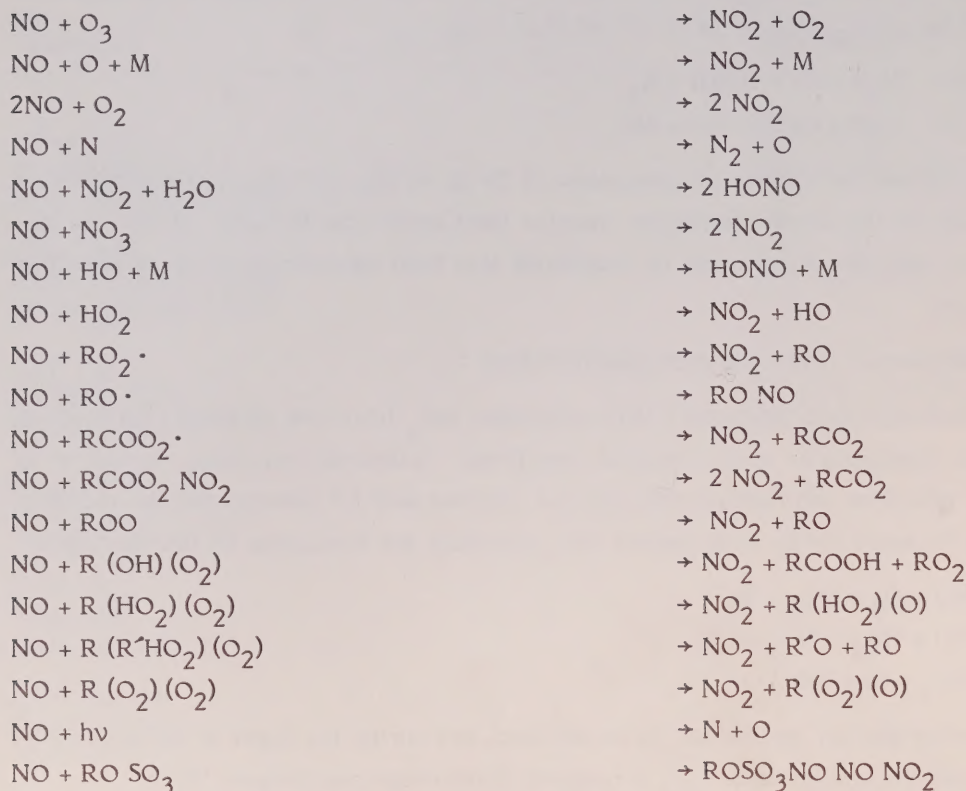
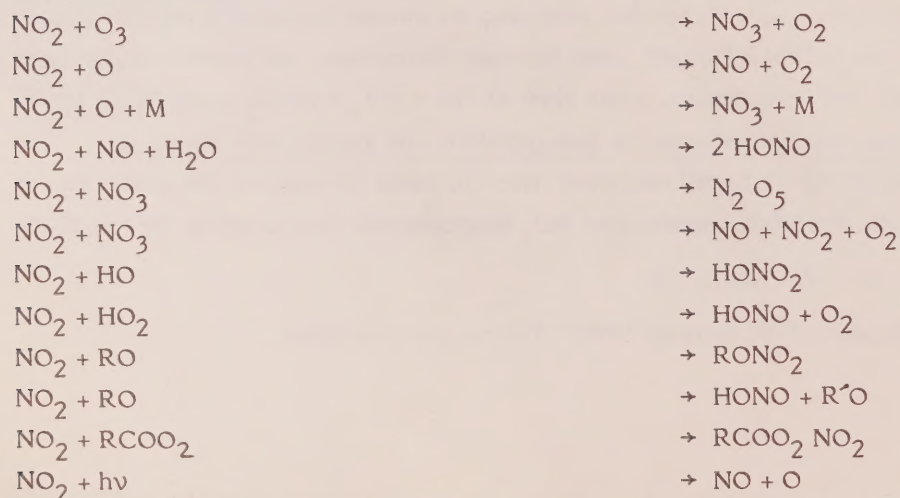


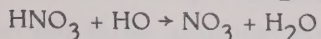
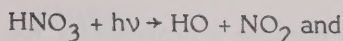
such that during the day equilibrium is established, but during the night in the absence of photolysis a net accumulation of NO_2 is realized (Bottenheim and Strausz 1977).

5.3.1 Atmospheric Fates. Atmospheric nitrogen oxide chemistry is extremely complex involving reactions with several oxidants, an almost limitless array of organic compounds, reactions with sulphur and other nitrogen compounds, and photolysis reactions (Table 15). Despite this complexity, a net flow of $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{HNO}_3$ exists, with HNO_3 being removed from the atmosphere by precipitative and particulate scavenging. For example, 13 of the 19 NO-initiated reactions listed in Table 15 result in the production of NO_2 . Excluding NO_2 photolysis, subsequent NO_2 reactions are dominated by the reaction:



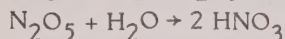
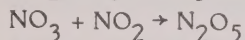
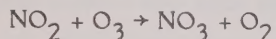
(Bottenheim and Strausz 1977, Graedel 1978). The reverse reactions,

TABLE 15 CHARACTERISTIC NO_x ATMOSPHERIC REACTIONSNO-Initiated ReactionsNO₂-Initiated Reactions



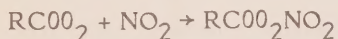
are slow and of little consequence (Bottenheim and Strausz 1977).

Reactions involving NO_2 and H_2O without OH oxidation are thought to proceed via the following reaction series:

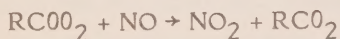


(Stoker and Seager, 1972, Rasmussen et al. 1975). Direct reaction of NO_2 with H_2O has been shown to be too slow to be of importance (Stoker and Seager 1972). Robinson and Robbins (1970) estimated from a global perspective that approximately 79% of NO_3^- formed in the above reactions is scavenged by precipitation, and the remaining 21% by dry deposition. Most of this NO_3^- is in the form of $\text{H}^+ \text{NO}_3^-$, but significant portions also occur as nitrate salts, principally NH_4NO_3 . Soderlund and Svensson (1976), on the other hand, concluded that dry deposition was the more important of the two processes, with wet deposition accounting for the removal of 18 to 46 Tg NO_3^- - N/yr globally, and dry deposition for 25 - 67 Tg NO_x - N/yr. Both forms of deposition are concentrated over land, and only a very small fraction of the material is deposited as particulates. Substantial portions of NO_x deposited in the absence of water are taken up directly by plants (Rogers et al. 1979).

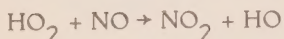
NO_x reactions involving organic gases are of particular concern because of the resultant photochemical smog produced in urban areas. The peroxyacetyl nitrates (PAN) so formed are typified by the reaction:



But not all peroxy radicals follow this reaction. Reactions involving NO result in the production of NO_2 via

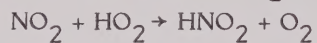
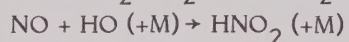
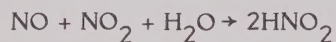


of which

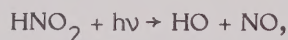


appears to be the most important reaction. Graedel (1977), however, has suggested that terpene reactions dominate peroxy radical series reactions where terpene emissions are significant.

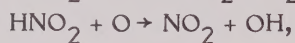
One last reaction series is of importance because it provides for the temporary storage of both NO and NO₂. This is the nitrous acid reactions series (Bottenheim and Strausz 1977):



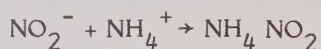
The HNO₂ so formed undergoes: (1) photolysis



or: (2) oxidation



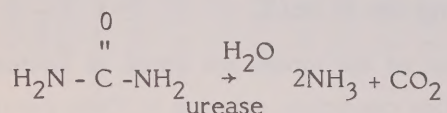
or: (3) nitrite salt formation in moisture-laden air



6 AMMONIA

6.1 Emission Sources and Flux Estimates

Among the natural sources that emit ammonia (NH_3) into the atmosphere are soils, vegetation, animal wastes, volcanos and geothermal steam (Graedel 1978). Of these, animal wastes and soils are the most important. Ammonia flux from soils results from the microbial breakdown of plant and animal proteinaceous materials. Ammonia flux from animal wastes is more direct, largely resulting from hydrolysis of urea by bacteria according to the equation



6.1.1 Terrestrial Biogenic Zones - Soils NH_3 flux from soils is dependent primarily on organic matter components, pH, temperature and moisture levels (Patrick and Wyatt 1964, Babich and Stotzky 1974, Paul and Victoria 1976, Dawson 1977). Available organic matter and temperature are, as might be expected, positively correlated with NH_3 flux. Moisture dependence is more complex. Soils with little or no moisture emit only small amounts of NH_3 . Those with low moisture levels emit comparatively large amounts of NH_3 as do saturated or near saturated soils, while soils with intermediate moisture levels emit lower concentrations (Dawson 1977). The effect of soil pH is such that soils of low pH (<6.0) emit little if any NH_3 (Junge 1958, Bouldin *et al.* 1974). Although some good general knowledge exists concerning the behaviour and emission of NH_3 as affected by different soil parameters, there exist to date few estimates of NH_3 flux from natural soil systems.

The most promising approach to the estimation of NH_3 flux from Canadian soil types lies in the employment of a model developed by Dawson (1977) to estimate NH_3 flux on the basis of readily available soil parameters. Proper testing of the model, unfortunately, has not occurred. Comments related to this fact are discussed at the end of the section. Dawson's model is as follows:

$$D = \frac{A D_o K B}{d \{H^+\}} f(\theta v) f'(T)$$

where:

D	=	total NH_3 flux ($\text{kg}/\text{m}^2/\text{s}$)
A	=	land surface area (m^2)
Do	=	diffusion coefficient of NH_3 in air ($0.24 \text{ cm}^2/\text{s}$)
K	=	constant = $2.04 \times 10^{-5} \text{ mol}\cdot\text{m}^2/\text{L}\cdot\text{kg}$
B	=	vegetation biomass (kg/m^2)
d	=	characteristic topsoil depth over which the NH_3 concentration gradient is established and is interpreted as being 10 cm
f(θ_v)	=	moisture function described in Dawson's text
f'(T)	=	temperature function described in Dawson's text
{H ⁺ }	=	hydrogen ion concentration in mol/L.

Soil parameters necessary to the application of the model are listed in Tables 3, 16 and 17. Verbal descriptions of soil and vegetation conditions relating to these parameters are described below. Monthly NH_3 fluxes from each soil group are shown in Table 18 immediately following the soil group descriptions.

6.1.1.1 Chernozemic soils. Chernozemic soils, distributed in the southern Prairies, are characterized by low moisture, neutral pH, and a comparatively high organic carbon content. Sand is the primary mineral particle size component, with silt and clay also being well represented (Table 3).

6.1.1.2 Solonetzic soils. Solonetzic soils are in many respects similar to chernozemic soils, except that upper layers are lower in pH, and structurally these soils are dominated by silt clay components (Table 3). Vegetation cover, like that of chernozemic soils, is composed primarily of grasses and forbs.

6.1.1.3 Luvisolic soils. This soil type is distributed primarily in portions of the Prairies, south-central British Columbia and in southern Ontario. Development of luvisolic soils has occurred mainly on glacial tills, glaciofluvial deposits and on glaciolacustrine deposits. The dominant vegetation type is Forest including Boreal, Montane, Deciduous and Great Lakes - Acadian Mixed Forest types. Moisture regimes are highly variable ranging from semiarid to humid. Nitrogen and organic contents of luvisolic soils tend to be low and mineral particle sizes are mainly in silt and sand phases.

6.1.1.4 Podzolic soils. Podzolic soils underlie most of the Boreal and Great Lakes - Acadian Mixed Forest areas from Saskatchewan to Newfoundland. They also show good

TABLE 16 WATER RETENTION CHARACTERISTICS OF MAJOR CANADIAN SOIL ORDERS

Soil Order	Estimated Ratio of Actual Annual Evaporation to Potential Annual ₁ Evaporation (E/E°)	Critical Moisture Volume Ratio (θ_v (crit))	Estimated Mean Annual Soil Volume Moisture Ratio
Chernozemic	0.5	0.202	0.101
Solonchic	0.6	0.259	0.155
Luvisolic	0.8	0.190	0.152
Podzolic	1.0	0.155	0.155
Brunisolic	1.0	0.245	0.245
Regosolic	1.0	0.234	0.234
Gleysolic	1.0	0.349	0.349
Organic	1.0	0.675	0.675
Rockland	-	-	-

1 Estimates derived from data presented by Strahler and Strahler (1978).

2 Estimates based on drainage data for sands, silts and clays at suction pressures of 75 cm as presented by Russell (1961, p. 381) with modification to account for mineral particle size proportions shown in Table 3.

TABLE 17 ADDITIONAL CRITICAL VALUES USED TO DETERMINE NH_3 FLUX FROM SOILS

Soil Order	ADoK/d ($\text{m}^5 - \text{mol/L} \cdot \text{kg} \cdot \text{s}$)	B (kg/m^2)	H^+ (mol/L)	f (θ_v)
Chernozemic	4.896×10^{-9}	2.5	7.94×10^{-8}	1.7
Solonetzic	4.896×10^{-9}	2.5	2.51×10^{-6}	1.5
Luvisolic	4.896×10^{-9}	33.0	2.00×10^{-6}	1.5
Podzolic	4.896×10^{-6}	33.0	1.58×10^{-4}	1.5
Brunisolic	4.896×10^{-9}	6.9	5.01×10^{-6}	0.6
Regosolic	4.896×10^{-9}	0.5	1.58×10^{-7}	0.7
Gleysolic	4.896×10^{-9}	10.0	1.26×10^{-7}	0.5
Organic	4.896×10^{-9}	11.1	1.58×10^{-5}	1.6
Rockland	4.896×10^{-9}			

Biomass estimations are from Krebs (1972, p. 449).

representation of west-facing slopes in southern British Columbia, but are of limited distribution elsewhere in Canada. Among the more prominent features of podzolic soils are low pH, high organic content, humid-to-prehumid moisture conditions and a predominance of sand-sized mineral particles. Because of the very low pH values exhibited by podzolic soils, NH_3 flux is extremely low.

6.1.1.5 Brunisolic soils. Soils of the brunisolic order occur under a wide variety of climatic and vegetative conditions. They are poorly developed and because of the strong heterogeneity exhibited, are difficult to characterize. In Canada, brunisolic soils are widely distributed in the Boreal Forest - Barrens of the Northwest Territories and throughout the Yukon, and in some mountainous areas of British Columbia. Distribution elsewhere is limited. The dominant vegetation type is therefore North Taiga-Sphagnum Bogs with Forest (Krebs 1972). For the most part, within limits of heterogeneity exhibited by this group, brunisolic soils tend to show a relatively low pH, subhumid-to-prehumid moisture conditions and a mixture of sand, silt and clay in which silt tends to be the predominant component.

6.1.1.6 Regosolic soils. Regosolic soils are with few exceptions confined mainly to the Tundra. They show negligible horizon development and tend to be characterized by near

TABLE 18 MONTHLY FLUXES OF NH_3 FROM CANADIAN SOIL ORDERS, BASED ON APPLICATION OF DAWSON'S (1977) NH_3 FLUX MODEL

Soil Order	$\frac{\text{ADoKB} \times f}{d \text{ H}^+}$ ($\text{g NH}_3 - \text{N/m}^2/\text{mo @ } 15^\circ\text{C}$)	April	May	June	July	August	September	October	Annual Flux ($\text{g NH}_3 - \text{N} \times 10^{-3}/\text{m}^2$)
Chernozemic	4.372×10^8	2.05	4.98	7.55	8.83	8.83	5.55	3.02	40.81
Solonchic	1.222×10^7	0.06	0.12	0.17	0.21	0.19	0.13	0.04	0.92
Luviosolic	2.022×10^8	0.16	2.11	3.06	3.94	3.49	2.31	0.95	16.02
Podzolic	2.559×10^6	-	0.02	0.04	0.05	0.05	0.03	0.01	0.20
Brunisolic	6.748×10^6	-	0.05	0.09	0.11	0.10	0.06	-	0.41
Regosolic	1.810×10^7	-	-	0.06	0.19	0.17	0.04	-	0.46
Gleysolic	3.241×10^8	-	2.24	5.22	6.02	5.22	3.06	0.26	22.02
Organic	9.179×10^6	-	0.06	0.13	0.17	0.14	0.09	0.02	0.61
Rockland									0.10
Mean Values		0.28	1.20	2.04	2.44	2.27	1.41	0.54	9.06
f' (T) values used in above calculations $\times 10^{-11}$									
1°C - 0.081	7°C - 0.814	13°C - 1.515							
2°C - 0.212	8°C - 0.945	14°C - 1.612							
3°C - 0.326	9°C - 1.042	15°C - 1.726							
4°C - 0.472	10°C - 1.140	16°C - 1.857							
5°C - 0.580	11°C - 1.270	17°C - 1.948							
6°C - 0.691	12°C - 1.401	18°C - 2.020							

neutral pH, humid conditions and a mixture of mineral particle sizes. However, conditions in the Arctic are highly variable and while the above constitutes a good approximation of average conditions, local conditions in many instances will be very different from those described.

6.1.1.7 Gleysolic soils. High moisture conditions and a high clay content characterize most gleysolic soils (Table 3). Vegetation developing on such sites is variable depending on location, but in most instances is dominated by northern Boreal Forests.

6.1.1.8 Organic soils. Peatland and other organic soil types are widely distributed in the Boreal - Barrens of northern Canada and in Boreal Forest sections of Alberta and Manitoba. These soils are unique in that they are composed almost solely of organic matter with little or no representation of sands, silts or clays in the upper layers. Drainage is poor and pH values tend to be low (Table 3).

6.1.1.9 Rockland. Soil development on rockland is generally poor, with the result that it is not possible to derive data necessary to the application of Dawson's (1977) model. However, considering that soils on rockland are thinly dispersed, that most rockland occurs in northern climates, and that underlying rocks are generally acidic, it is probable that rocklands emit less NH_3 than any of the other soil types described above. Emission fluxes are tentatively estimated at $0.100 \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{yr}$.

6.1.1.10 Ammonia fluxes from soils: comparison with other sources. Several authors have discussed NH_3 evolution from soils, but few field measurements are available. Barsdate and Alexander (1975), for example, considered that NH_3 emissions from Tundra soils were of limited significance because of low pH, wetness and low temperatures. Most researchers have concluded that NH_3 flux is minimal from soils with $\text{pH} < 6.0$ (Junge 1958, Bouldin et al. 1974). But Bartlett et al. (1979), working with soil suspensions, presented data showing a reverse trend. Experimental methods make comparisons between their data and those of other researchers difficult.

Field measurements have been presented by Kim (1973) for natural systems and by Denmead et al. (1976) for pastured areas. Denmead et al. (1976) measured NH_3 flux from an ungrazed pasture in Australia during November to be approximately $146 \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{mo}$, with a range of $(0 - 192) \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{mo}$. This value is approximately three times the value calculated for chernozemic soils using Dawson's (1977) model. Moreover, pH of the upper soil layer was measured at 6.0 indicating that comparative fluxes are even more disproportionate. Also Denmead et al.

(1976) found that actual fluxes from soil averaged $1737.4 \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{mo}$, but that approximately 92% of this flux was absorbed directly by the vegetation canopy consisting of grasses and forbs, and was thus prevented from escaping into the atmosphere. Allowing for differences in pH, the NH_3 flux from the Australian grassland plot into the atmosphere is approximately fifty times that predicted by Dawson's (1977) model.

Results presented by Kim (1973) for a sod area in southern Korea, with soil and climatic conditions similar to those of southern Ontario's luvisolic soils, showed a monthly summer flux of approximately $657 \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2$. Adjusting these data to account for pH differences such that comparisons can be made with Canadian Prairie grasslands, Kim's estimates exceed those predicted by Dawson's (1977) model by a factor of about 1800. Fluxes from forested communities of the same soil type, measured by Kim (1973), were about 1.6 times those measured for grassland.

Dawson's (1977) model ignored the contribution of NH_3 from animal wastes which could in part account for the lower flux estimates. But, NH_3 fluxes from a grazed pasture with a density of 22.5 sheep per hectare resulted in an average $\text{NH}_3\text{-N}$ flux of $949 \times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{mo}$, a value only 6.5 times that found for ungrazed pasture (Denmead et al. 1976). Dawson (1977) dismissed the results of Denmead et al. (1976) as being from an enriched as opposed to a natural system. He concluded that there were no flux measurements available with which to compare results from the model.

On the basis of the above comparisons it would appear that estimates of NH_3 flux derived from Dawson's (1977) model are at least an order of magnitude less than observed field results. NH_3 fluxes from Canadian soils are therefore amended as follows ($\times 10^{-3} \text{ g NH}_3 - \text{N/m}^2/\text{yr}$):

Soil Order	Flux
Chernozemic	408.1
Solonetzic	9.2
Luvisolic	160.2
Podzolic	2.0
Brunisolic	4.1
Regosolic	4.6
Gleysolic	220.2
Organic	6.1
Rockland	1.0

6.1.2 Terrestrial Biogenic Zones - Vegetation. Farquhar et al. (1978) were the first researchers to conclude that NH_3 is volatilized from plants. Working with corn plants they calculated a daily flux from senescing leaves, under laboratory conditions, of 7 g NH_3 -N/ha. Details showing the derivation of this estimate are not provided. Whether or not other plants act as an NH_3 source is unclear. Given that senescence is a biological decay process, it is likely that it is a source. However, Denmead et al. (1976) have shown that under normal conditions, plants act as a sink for NH_3 , absorbing as much as 92% of NH_3 -N released by soils. In view of the above, plants are considered to be net sinks for NH_3 . Moreover, the majority of NH_3 released from senescing material is included in NH_3 flux estimates from soils.

6.1.3 Terrestrial Biogenic Zones - Forest and Brush Fires. The extreme oxidizing potential of fires precludes NH_3 volatilization from this source.

6.1.4 Terrestrial Biogenic Zones - Animal Wastes. Healy et al. (1970) considered animal urine to be without question the most important source of NH_3 volatilized into the atmosphere. He estimated that urea production by domestic herbivores averaged approximately 0.45 g of urea per kg of animal per day. Assuming that 10% of this is volatilized as NH_3 (Healy et al. 1970), total NH_3 production from herbivores is in the order of 0.037 g NH_3 - N per kg of animal per day.

Other studies have indicated that considerable amounts of NH_3 are volatilized from manure (Lauer et al. 1976), but the manure used included urine. Compared to NH_3 production from urine, production from fecal matter is negligible.

Carnivorous mammals, because they have high-protein diets, excrete considerably greater amounts of urea per unit weight than do herbivores. Data suitable to estimates of urea production from carnivores are provided by Golley et al. (1965). These authors measured urine excretion from bobcats (medium-sized carnivores) to be approximately 42 g of urine per kg of animal per day. Urea concentrations in feline urine have been estimated at 120 g/L (Schmidt-Nielsen 1964). Assuming 10% of this urea is volatilized as NH_3 , total NH_3 production from carnivores is estimated at approximately 0.42 g NH_3 - N per kg of animal per day.

Estimates of the number of wild herbivorous mammals in Canada can be derived from data presented by Peterson (1955), Banfield (1974), Rue (1978) and others, and from Canadian fur returns assuming that 10% and 5% of Canada's beaver and muskrat

populations, respectively, are trapped annually (Table 19). Estimates of cattle and sheep numbers are available from Statistics Canada (Table 19).

The total estimated annual emission of NH_3 from wild herbivorous mammals in Canada is approximately 2.02×10^{10} g NH_3 -N. By dividing the country into major biotic regions and estimating the relative herbivore biomass density, one can estimate NH_3 emissions from wild herbivores on a per unit area basis (Table 20). But these estimates do not include uric acid production from herbivorous invertebrates or birds, which are likely to double the values shown. Nor do they include production from predators.

Predator-prey biomass ratios are normally in the 1:100 to 1:500 range. Taking an average value of 1:300 and assuming an NH_3 -derived emission of 0.42 g NH_3 - N per kg of predator per day as calculated above, then the increased amount of NH_3 flux over that produced by herbivores would be $(0.42/0.037) \times (1/300) = 3.8\%$.

Also assuming that approximately 85% of domestic herbivores are in Grassland-Agricultural Zones and that 5% are in each of Coastal-Mountain, Great Lakes - Acadian, and Aspen Parkland biomes, then the following estimates of NH_3 flux from domestic herbivores are obtained (g NH_3 -N/m²/yr):

Grassland - Agriculture	0.1872
Coastal - Mountain Forests	0.0070
Great Lakes - Acadian Forests	0.0087
Aspen Parkland	0.0209

NH_3 emissions from all animal sources on a biome per unit area basis are therefore estimated at (g NH_3 -N/m²/yr):

Tundra	0.00166
Boreal Forest - Barrens	0.00247
Boreal Forest	0.00498
Aspen Parkland	0.03786
Coastal - Mountain Forests	0.01699
Great Lakes - Acadian Forests	0.01698
Grassland - Agriculture Zones	0.20040

6.1.5 Aquatic Biogenic Zones - Freshwater. While fish and other aquatic organisms unquestionably emit nitrogen compounds that are subsequently broken down into ammonia products by bacteria and other microorganisms, data provided by Luebs *et al.* (1973), Viets (1974) and others, indicate that aquatic environments have a large capacity to absorb

TABLE 19 ESTIMATED NH_3 EMISSIONS FROM WILD AND DOMESTIC HERBIVOROUS CANADIAN MAMMALS

Group/Species	Estimated Canadian Population	Approximate Individual Wt. (kg)	NH_3 Emissions per kg of animal/yr (g NH_3 - N)	Total Emissions (g NH_3 - N/yr)
Deer	1 590 000	75	13.5	1.61×10^9
Moose	250 000	400	13.5	1.35×10^9
Elk	200 000	270	13.5	0.73×10^9
Caribou	300 000	95	13.5	0.38×10^9
Musk Ox	10 000	315	13.5	0.43×10^8
Pronghorn Antelope	40 000	45	13.5	0.24×10^8
Bighorn Sheep	5 000	120	13.5	0.08×10^8
Mice and Voles	20 000 000 000	0.035	13.5	0.94×10^{10}
Hares and Rabbits	250 000 000	1.5	13.5	0.51×10^{10}
Beaver	4 000 000	20	13.5	0.11×10^{10}
Muskrat	30 000 000	1.1	13.5	0.45×10^9
Cattle	15 000 000	400	13.5	8.10×10^{10}
Sheep	670 000	50	13.5	0.45×10^9
				10.16×10^{10}

TABLE 20 ESTIMATED NH_3 FLUXES ON A PER UNIT AREA BASIS FOR MAJOR BIOMES
DERIVED FROM WILD MAMMALIAN HERBIVORES

Biome	Approximate Area in Canada (km^2)	Relative Herbivore Density	Estimated Flux ($\text{g NH}_3 - \text{N}/\text{m}^2/\text{yr}$)
Tundra	3 700 000	1.0	0.00080
Boreal Forest - Barrens	2 100 000	1.5	0.00119
Boreal Forest	2 500 000	3.0	0.00240
Aspen Parkland	200 000	10.0	0.00817
Coastal - Mountain Forests	590 000	6.0	0.00481
Great Lakes - Acadian Forests	470 000	5.0	0.00399
Grassland - Agriculture	370 000	8.0	0.00636
	<u>9 930 000</u>		

NH_3 . Consequently, aquatic biogenic zones act as a net sink for, and not a net source of, atmospheric NH_3 .

6.1.6 Aquatic Biogenic Zones - Marine Waters. Arguments presented above also apply to marine waters.

6.1.7 Production From Lightning. The strong oxidizing environment produced by lightning precludes the formation of NH_3 .

6.2 Atmospheric Concentrations

As a result of differing source strengths and because of varying scavenging rates, atmospheric NH_3 concentrations are highly variable. Agricultural areas in particular exhibit high atmospheric concentrations. For example, Luebs *et al.* (1973) reported concentrations of up to $69 \mu\text{g NH}_3 - \text{N/m}^3$ in an area populated by 1600 head of cattle per km^2 . Average values from areas not so populated ranged from <0.59 to $22.90 \mu\text{g NH}_3 - \text{N/m}^3$, with a mean value of 7.0. Marine atmospheres exhibit lower concentrations, averaging $3.55 \mu\text{g NH}_3 - \text{N/m}^3$ (Table 21). From the little data available it appears that NH_3 concentrations in tropical air masses are higher than those of temperate zones (Lodge *et al.* 1974).

In addition to the more obvious seasonal and diurnal effects of temperature on NH_3 flux into the atmosphere, a number of other factors are also known to affect temporal NH_3 concentrations. Among these are precipitation which quickly removes NH_3 from the atmosphere, a result of the high solubility of this gas in water, and weather fronts which alternate air masses subject to varying NH_3 source strengths. Vertical profiles of NH_3 concentrations in the atmosphere have been studied in depth by McConnel (1973). His models indicate that NH_3 mixing ratios are relatively stable up to an altitude of about 15 km at which point concentrations decrease dramatically, reaching negligible values at 30 km.

6.3 Residence Times and Atmospheric Fates

6.3.1 Residence Times. Estimates of the atmospheric lifetime of NH_3 show comparatively little variation, ranging from 20 to 30 days (Tsunogai 1971, McConnel and McElroy 1973, Graedel 1978). In view of observed variabilities in scavenging rates by precipitation and other mechanisms, this consistency is surprising.

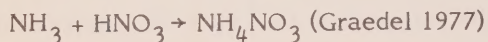
6.3.2 Atmospheric Fates. There is consensus in the literature, despite some irregularities, that absorption by precipitation, water and land surfaces, and vegetation

TABLE 21 BACKGROUND ATMOSPHERIC CONCENTRATIONS OF NH_3 IN
CLEAN AIR ($\mu\text{g NH}_3 - \text{N/m}^3$)

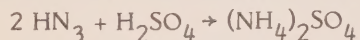
Terrestrial	Marine	Assumed Global Average
2 - 6 Florida Junge (1956)	0.52 - 3.22 Hawaii Junge (1957)	3.3 - 16.5 Georgii (1963)
0.59 - 5.92 Central United States Breeding <u>et al.</u> (1973)	0.03 - 0.60 South Pacific Tsunogai (1971)	3.6 Robinson and Robbins (1970)
3 California Luebs <u>et al.</u> (1973)	0.25 - 0.82 North Sea Georgii and Muller (1974)	2.5 - 4.1 Georgii and Muller (1974)
7 - 18 Western Germany Georgii and Muller (1974)	5.16 - 17.77 American tropics Lodge <u>et al.</u> (1974)	1.18 - 4.15 Graedel (1977)
1.72 - 22.9 American tropics Lodge <u>et al.</u> (1974)		

constitute the primary sinks for NH_3 . In many instances, absorption is preceded by chemical reactions, the most important of which appears to be:

(M)



In polluted atmospheres, the following reaction may be significant:



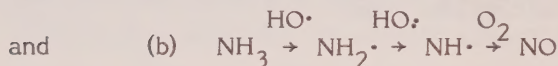
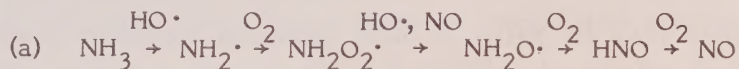
Since all such removal mechanisms are climate dependent, it is to be expected that the atmospheric fate of NH_3 will exhibit considerable variability, with dry deposition taking a greater precedence in drier climates than in more humid biomes.

Comparative global estimates of the amount of NH_3 ultimately removed by dry and wet deposition have been provided by McConnel (1973) and by Soderlund and Svensson (1976). The latter authors considered that wet deposition accounted for the annual removal of from 8 to 25, and 30 to 60 Tg N of ammonium compounds over ocean

and land areas, respectively. Greater atmospheric losses were attributable to dry decomposition, with annual losses of $\text{NH}_3\text{-N}$ over ocean and land areas estimated at 10 to 20, and 57 to 114 Tg, respectively. Particulate ammonium compounds removed from the atmosphere by dry deposition processes were estimated at from 1 to 5, and 4 to 12 Tg N annually for ocean and land areas, respectively. Similar results attaching a greater importance to dry deposition were reported by McConnel (1973).

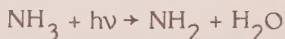
Further to the process of dry deposition, several studies have shown that the potential for absorption considerably exceeds the demand placed on these systems. For example, Viets (1974) observed that water surfaces under normal agricultural conditions absorbed some 3.9 kg of $\text{NH}_3\text{-N}$ per hectare of water surface per year, but that up to 73 kg $\text{NH}_3\text{-N/ha/yr}$ were absorbed close to a cattle feedlot. Luebs *et al.* (1973) reported even higher absorption potentials of 190 kg $\text{NH}_3\text{-N/ha/yr}$. Perhaps more striking are the results of Denmead *et al.* (1976), who observed that approximately 92% of NH_3 volatilized from the soil surface of an ungrazed grassland area was reabsorbed by the plant canopy, thus never reaching the open atmosphere.

With regard to atmospheric reaction systems, Graedel (1977) considered the reaction of NH_3 with HNO_3 yielding NH_4NO_3 to be the most important. This reaction accounts for an estimated removal of 10^{-5} ppm $\text{NH}_3\text{/min}$ during daylight hours. The next most important reaction series considered were:

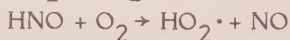
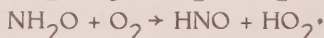


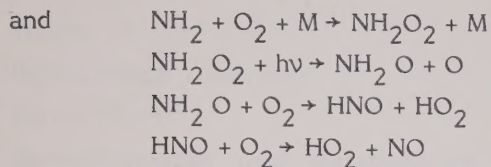
Reactions a and b above account for the removal of 10^{-7} ppm $\text{NH}_3\text{/min}$ during daylight hours. Aerosol removal mechanisms were considered the least important.

One last reaction warranting consideration is stratospheric NH_3 photolysis:

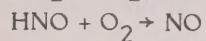
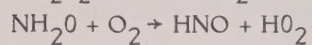
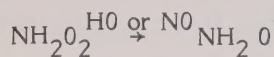
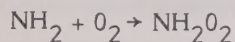


Subsequent possible reactions postulated by McConnel and McElroy (1973) leading to the eventual production of NO are:





Graedel (1977), however, proposed the following reaction series:



None of these reactions appears to be very fast. Alternatively, NH_2 can react with NO to yield $\text{N}_2 + \text{H}_2\text{O}$ (Bottenheim and Strausz 1977).

7 AMINES

7.1 Emission Sources and Flux Estimates

Several amines have been identified as emanating from natural sources, primarily from animal wastes, but also from vegetation and from microbes (Graedel 1978). Unfortunately, the only flux estimates available are those from animal waste. Elliott *et al.* (1971) found that non-distillable nitrogen from cattle feedlots accounted for 0.088% of the total nitrogen evolved, or 0.097:1 relative to NH_3 -N. These authors presumed that the components being evolved were amines and also possibly heterocyclic compounds, but no identifications were attempted. A more detailed analysis of non-distillable nitrogen containing compounds evolved from cattle feedlots is provided by Mosier *et al.* (1973). These authors identified the following quantities of amine-N evolved relative to NH_3 - N:

Methylamine	0.00339
Dimethylamine	0.00093
Ethylamine	0.00467
n-Propylamine	0.00071
Isopropylamine	0.00180
n-Butylamine	0.00014
n-Pentylamine	0.00012

yielding a total amine-N production of 0.012 relative to NH_3 - N. Assuming that non-distillable nitrogen compounds detected by Elliott *et al.* (1971) were similar in proportion to the above, total amine - N evolved relative to NH_3 - N averaged over the two studies is 0.0545. Whether or not these amines are emitted in similar proportions under more natural conditions has not been determined. There is some evidence that nitrogen compounds evolved from feedlots behave differently from those evolved under more natural conditions, because of the marked difference in animal concentrations (Soderlund and Svensson 1976 citing Eriksson 1959). However, until better data are available it is assumed that amines are emitted under natural or quasi-natural conditions in proportions similar to those tabulated above.

Amine fluxes from all animal sources on a biome per unit area basis, using data developed in Section 6.1.4 pertaining to NH_3 flux, are therefore estimated at (g amine - N/m²/yr):

Tundra	0.090×10^{-3}
Boreal Forest - Barrens	0.134×10^{-3}
Boreal Forest	0.271×10^{-3}
Aspen Parkland	2.060×10^{-3}
Coastal - Mountain Forests	0.924×10^{-3}
Great Lakes - Acadian Forest	0.924×10^{-3}
Grassland - Agriculture Zones	10.901×10^{-3}

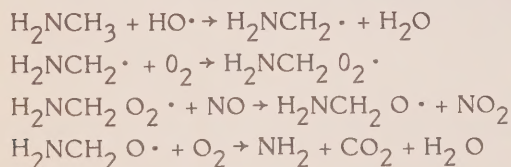
7.2 Atmospheric Concentrations

So far as we are aware there are no estimates of ambient concentrations of amines in clean air environments.

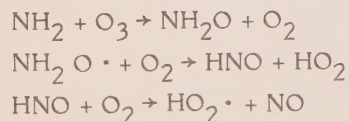
7.3 Residence Times and Atmospheric Fates

Comparatively little information is available on either residence times or atmospheric fates of amines. Graedel (1978) lists lifetimes of methylamine, dimethylamine and ethylamine, based on reactions with hydroxyl radicals, at 28, 11 and 24 hours, respectively.

Atmospheric reactions of amines are thought to include hydroxyl abstraction reactions similar to those experienced by organic compounds (Graedel 1978), and reactions with nitrous acid (Hanst et al. 1977). Assuming that amine hydroxyl series reactions are similar to those experienced by organic compounds, then the following reaction series is most plausible:

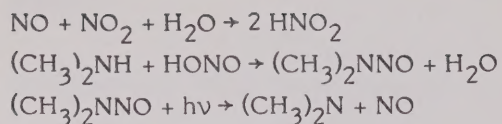


Subsequent reactions series suggested by McConnel and McElroy (1973) result in the production of NO:



Alternatively, NH_2 can react with NO to yield N_2 and H_2O (Bottenheim and Strausz 1977).

Nitrous acid reactions yield N-nitroso amines:



which is apparently then oxidized through an unknown series of reactions to yield CO and H_2CO .

The relative effectiveness of the above alkyl amine sink compared to that provided by precipitative and other scavenging processes has not been determined. But given the high solubilities of alkyl amines in water (Table 1), it appears probable that considerable portions of these compounds are removed by precipitative scavenging and by surface absorption by water, land and other surfaces.

8 PARTICULATE NITROGEN COMPOUNDS

8.1 Emission Sources and Flux Estimates

Atmospheric nitrogen particulates are derived from materials carried aloft by air currents, principally soil particles and water droplets, and from atmospheric reactions involving gases and/or their ionic derivatives in vapour phase hydrologic environments. Resulting particulate loadings are highly variable depending on available materials, wind speeds, moisture levels, ground cover and terrain. But so far as we are aware there are no estimates in the literature of nitrogen particulate flux from natural sources other than those derived from secondary atmospheric reactions such as that between NH_3 and HNO_3 .

Generalized estimates of nitrogen ion flux from marine environments can be derived by comparing relative nitrogen ion concentrations to salt flux. Salt flux production from the oceans has been estimated at 5.54×10^{11} g/yr (Gross 1972, p. 163). Approximately 30.6% of this salt flux by weight is Na^+ , yielding a global oceanic Na^+ flux of 1.53×10^{-3} g Na^+ /m²/yr. Marine concentrations of Na^+ are in order of 1.05×10^7 µg/L (Gross 1972, p. 398). NO_3^- concentrations in Canadian surface waters range from 0.03 to 16 µg NO_3^- - N/L (Cattell 1973, Grainger and McSween 1976, Denman *et al.* 1977, Grainger 1974, Irwin *et al.* 1978, Coote and Yeates 1979), with maximum values observed during winter months. Assuming that NO_3^- ions have similar per unit fluxes compared to Na^+ ions, then maximum NO_3^- fluxes would be in the order of:

$$\begin{aligned} & \frac{1.6 \times 10^1}{1.05 \times 10^7} \times 0.77 \times 10^{-3} \text{ g } \text{NO}_3^- \text{ - N/m}^2/\text{yr} \\ & = 1.2 \times 10^{-9} \text{ g/m}^2/\text{yr} \end{aligned}$$

NO_3^- fluxes from marine waters are therefore regarded as negligible. Marine concentrations of nitrite ions are generally less than those of NO_3^- , and NH_4^+ ion concentrations are less than an order of magnitude larger than NO_3^- concentrations.

From the above, it is concluded that almost all aerosol nitrogen components emitted into the atmosphere are derived from, or attached to, airborne soil particles. This conclusion is in agreement with findings presented by Moore (1974). No flux estimates are available for nitrogen particulates, but it would appear on the basis of relative atmospheric concentrations that fluxes are small.

8.2 Atmospheric Concentrations

Background concentrations of NO_3^- and NH_4^+ (Table 22) are generally less than those reported for NO_2 and NH_3 . Somewhat surprisingly, concentration differences between land and sea air masses appear small, but data are few. Data relating to deposition rates presented by Warneck (1974), however, indicate that ambient concentrations of NO_3^- over continents are an order of magnitude larger than those found in marine air masses.

8.3 Residence Times and Atmospheric Fates

Aerosol lifetimes are strongly influenced by climatic conditions, particularly wind, rain and convectional turbulence. Consequently, it is difficult to estimate lifetimes in a form comparable to those computed for gaseous compounds. Nevertheless, estimates of turnover times for ammonium and nitrate compounds on a global basis have been computed as 7 to 19 days, and 4 to 20 days, respectively (Soderlund and Svensson 1976). Tentative estimates put forward for lifetimes of organic nitrogen particulates by these authors are in the order of 10 days. In all cases, precipitation is considered to be the most important removal agent.

Regarding atmospheric fates, Robinson and Robbins (1970) estimated that approximately 79% of NO_3^- aerosols were removed from the atmosphere by precipitative scavenging, with the remainder being removed by dry deposition. Similar values have been reported by Soderlund and Svensson (1976). Other potential sinks for nitrogen aerosols include chemical and absorption reactions, and transport to the stratosphere. But in comparison to precipitative scavenging and dry deposition, these sinks are unimportant.

TABLE 22 BACKGROUND ATMOSPHERIC CONCENTRATIONS OF NO_3^- AND NH_4^+ IN CLEAN AIR (g N/m^3)

Terrestrial	Marine
Nitrate (NO_3^-)	
0.35	0.09
Florida	Hawaii
Junge (1956)	Junge (1957)
0.04 - 0.12	0.0 - 0.4
Colorado	Mid-Pacific
Moore (1974)	Lodge <u>et al.</u> (1960)
0.2	
Southern Germany	
Reiter <u>et al.</u> (1974)	
0.01 - 0.4	0.23
Scandinavia	North Sea
Soderlund and Svensson (1976)	Georgii and Muller (1974)
Ammonium (NH_4^+)	
0.12	0.04
Florida	Hawaii
Junge (1956)	Junge (1957)
0.05 - 0.48	
Colorado	
Moore (1974)	

9 SUMMARY OF ANNUAL EMISSIONS OF NITROGEN COMPOUNDS IN CANADA

9.1 Terrestrial Zone Emissions

In order to be consistent with other reports in the series on natural emissions, estimates of nitrogenous gas fluxes are presented on the basis of Canadian census divisions. Distributions of major soil and biome types used to compute fluxes in each of the census divisions were determined from planimetry and dot-grid techniques. These data, together with flux estimates calculated in Sections 4 to 7 and summarized in Table 23, were then employed to derive emission estimates of N_2O , NO_x , NH_3 and amines from census divisions.* Provincial and territorial summaries of flux estimates for the above compounds are listed in Table 24. A detailed provincial summary of estimated emissions by source, for each of the nitrogen compounds is given in Tables 25 to 36.

Data from Table 23 show that soils, animal wastes, lightning and oceans are the dominant nitrogen emission sources. In most of eastern Canada where the amount of agricultural land is comparatively small, and where podzolic and to a lesser extent organic soils are widespread, nitrogen emissions are dominated by N_2O and NO_x (Table 24). In western Canada considerable areas of land are used to raise livestock. Moreover, these areas are underlain to a large extent by chernozemic and luvisolic soils with the result that nitrogen emissions in western Canada are dominated by NH_3 (Table 24). In Manitoba and British Columbia, however, emissions of NO , NO_x and NH_3 are similar in magnitude. In the Yukon and Northwest Territories nitrogen emissions are dominated by N_2O and NO_x , but not to the same extent as in eastern Canada. Amine emissions from all areas are comparatively small.

As an objective assessment of emission strengths derived in this study, emission ratios obtained can be compared to those from published global nitrogen budgets. Emission ratios based on flux of N_2O , NO_x and NH_3 from Canadian terrestrial environments, as determined in this study, are:

$$\begin{array}{rcccl} N_2O - N & : & NO_x - N & : & NH_3 - N \\ 1.4 & : & 1.5 & : & 1.0 \end{array}$$

*This detailed information can be obtained upon request from Environment Canada, Air Pollution Control Directorate; Pollution Data Analysis Division, Ottawa, Ontario, K1A 1C8.

TABLE 23 NITROGEN FLUXES FROM CANADIAN ENVIRONS (kg N/km²/yr)

Source	Species or Compound Class			
	N ₂ O	NO _x	NH ₃	Amines
Terrestrial Biogenic Zones				
Soils:				
Chernozemic	107.4	2.6	408.1	
Solonetzic	44.9	12.2	9.2	
Luvisolic	27.2	5.8	160.2	
Podzolic	225.4	272.8	2.0	
Brunisolic	47.0	20.0	4.1	NA/N
Regosolic	6.7	0.4	4.6	
Gleysolic	26.3	0.7	220.2	
Organic	157.9	156.4	6.1	
Rockland	5.0	0.3	1.0	
Vegetation:	NA/N	NA/N	NA/N	NA/N
Forest and Brush Fires:				
Tundra	-	-		
Boreal Forest - Barrens				
Ont. -Que. -Mar.	0.27	0.28		
Prairies-Terr.	0.49	0.52		
Boreal Forest				
Ont. -Que. -Mar.	1.05	1.13		
Prairies-Terr.	1.96	2.09	NA/N	NA/N
Aspen Parkland	0.98	1.04		
Coastal - Mountain Forests	0.49	0.52		
Great Lakes - Acadian Forests	1.26	1.35		
Grassland - Agriculture	0.02	0.02		
Animal Wastes:				
Tundra			1.66	0.09
Boreal Forest - Barrens			2.47	0.13
Boreal Forest			4.98	0.27
Aspen Parkland	NA/N	NA/N	37.86	2.06
Coastal - Mountain Forests			16.99	0.92
Great Lakes - Acadian Forests			16.98	0.92
Grassland - Agriculture			200.40	10.90

TABLE 23 NITROGEN FLUXES FROM CANADIAN ENVIRONS (kg N/km²/yr)
(Cont'd.)

Source	Species or Compound Class			
	N ₂ O	NO _x	NH ₃	Amines
Aquatic Biogenic Zones:				
Freshwater	NA/N	NA/N	NA/N	NA/N
Marine				
Arctic	29.0			
Pacific	101.0	NA/N	NA/N	NA/N
Atlantic-south	84.0			
Atlantic-north	59.0			
Lightning:				
Tundra	0.05	2.72		
Boreal Forest - Barrens	0.19	10.36		
Boreal Forest	0.39	20.71		
Aspen Parkland	0.62	33.16		
Coastal - Mountain Forests	0.27	14.35		
Great Lakes - Acadian				
Forests	0.54	28.71		
Grassland - Agriculture	0.67	35.88		

NA/N - flux estimates not available or negligible.

TABLE 24 ESTIMATED ANNUAL FLUXES OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)

Province/Territory	Species or Compound Class				Total
	N ₂ O	NO _x	NH ₃	Amines	
Newfoundland	40.801	52.484	1.975	0.061	95.321
Nova Scotia	9.032	12.038	2.981	0.048	24.099
Prince Edward Island	1.279	1.749	1.143	0.062	4.233
New Brunswick	12.236	16.300	4.217	0.064	32.817
Quebec	168.436	214.649	18.276	0.586	401.947
Ontario	135.070	165.878	52.432	0.974	354.354
Manitoba	70.377	73.713	60.815	0.383	205.288
Saskatchewan	69.472	65.027	110.700	0.810	246.009
Alberta	45.614	39.485	115.228	1.278	201.605
British Columbia	63.304	70.740	60.978	0.550	195.572
Yukon	18.739	15.281	8.389	0.106	42.515
Northwest Territories	97.759	91.328	33.393	0.336	222.816
Canada	732.119	818.672	470.527	5.258	2026.576

TABLE 25 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- NEWFOUNDLAND

Province	Emission Source	Area (km ²)	Species or Compound Class					Total
			N ₂ O	NO _x	NH ₃	Amines		
Nfld.	S* - Podzolic	168 924	38.012	46.120	0.338		84.470	
	Luvisolic	1 830	0.050	0.011	0.290		0.351	
	Organic	10 192	1.610	1.590	0.062		3.262	
	Rockland	175 826	0.879	0.053	0.176		1.108	
	Sub-total		40.551	47.774	0.866		89.191	
F -	Boreal F.	98 124	0.102	0.111			0.213	
	Boreal B.	235 681	0.064	0.066			0.130	
	Tundra	22 985						
	Sub-total		0.166	0.177			0.343	
W -	Boreal F.	98 124			0.489	0.027	0.516	
	Boreal B.	235 681			0.582	0.032	0.614	
	Tundra	22 985			0.038	0.002	0.040	
	Sub-total				1.109	0.061	1.170	
L -	Boreal F.	98 124	0.038	2.029			2.067	
	Boreal B.	235 681	0.045	2.441			2.486	
	Tundra	22 985	0.001	0.063			0.064	
	Sub-total		0.084	4.533			4.617	
Total			40.801	52.484	1.975	0.061	95.321	

*In Tables 25 to 36, the following symbols are used: S - soils; F - forest and brush fires;
W - animal wastes; and L - lightning.

TABLE 26 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x10⁶/yr)
- NOVA SCOTIA

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
N.S.	S - Podzolic	38 195	8.591	10.422	0.076		19.089
	Luvisolic	12 691	0.345	0.075	2.031		2.451
	Regosolic	397	0.003		0.002		0.005
	Sub-total		8.939	10.497	2.109		21.545
	F - G.L.-Acad.	51 277	0.065	0.069			0.134
	W - G.L.- Acad.	51 277			0.872	0.048	0.920
	L - G.L.-Acad.	51 277	0.028	1.472			1.500
Total			9.032	12.038	2.981	0.048	24.099

TABLE 27 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- PRINCE EDWARD ISLAND

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
P.E.I.	S - Podzolic	5 660	1.274	1.545	0.011		2.830
	F - Grass Agr.	5 660	0.001	0.001			0.002
	W - Grass Agr.	5 660			1.132	0.062	1.194
	L - Grass Agr.	5 660	0.004	0.203			0.207
Total			1.279	1.749	1.143	0.062	4.233

TABLE 28 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUND (kg N x 10⁶/yr)
- NEW BRUNSWICK

Province	Emission Source	Area (km ²)	Species or Compound Class				
			N ₂ O	NO _x	NH ₃	Amines	Total
N.B.	S - Podzolic	51 596	11.612	14.087	0.104		25.803
	Luvisolic	18 274	0.498	0.107	2.923		3.528
	Regosolic	146	0.001		0.001		0.002
	Sub-total		12.111	14.194	3.028		29.333
	F - G.L.-Acad.	70 015	0.087	0.094			0.181
	W - G.L.-Acad.	70 015			1.189	0.065	1.254
	L - G.L.-Acad.	70 015	0.038	2.011			2.049
	Total		12.236	16.299	4.217	0.065	32.817

TABLE 29 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- QUEBEC

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Que.	S - Luvisolic	12 613	0.343	0.073	2.021		0.637
	Podzolic	672 655	151.616	183.500	1.345		336.461
	Brunisolic	33 854	1.591	0.677	0.139		2.337
	Gleysolic	13 991	0.368	0.010	3.081		3.459
	Organic	72 176	11.397	11.288	0.440		23.125
	Rockland	425 928	2.130	0.128	0.426		2.684
	Sub-total		167.445	195.676	7.452		370.573
	F - Tundra	211 215					
	Boreal B.	418 374	0.113	0.117			0.230
	Boreal F.	467 004	0.490	0.528			1.018
	G.L.-Acad.	94 435	0.046	0.049			0.095
	Grass Agr.	27 494	0.001	0.001			0.002
	Sub-total		0.650	0.695			1.345
	W - Tundra	211 215			0.351	0.019	0.370
	Boreal B.	418 374			1.033	0.054	1.087
	Boreal F.	467 004			2.326	0.126	2.452
	G.L.-Acad.	94 435			1.604	0.087	1.691
	Grass Agr.	27 494			5.510	0.300	5.540
	Sub-total				10.824	0.586	11.410
	L - Tundra	211 215	0.011	0.575			0.586
	Boreal B.	418 374	0.079	4.334			4.413
	Boreal F.	467 004	0.182	9.672			9.854
	G.L.-Acad.	94 435	0.051	2.711			2.762
	Grass Agr.	27 494	0.018	0.986			1.004
	Sub-total		0.341	18.278			18.619
	Total		168.436	214.649	18.276	0.586	401.947

TABLE 30 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- ONTARIO

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Ont.	S - Podzolic	397 806	89.666	108.521	0.796		198.983
	Brunisolic	29 875	1.404	0.598	0.122		2.124
	Rockland	15 787	0.679	0.005	0.016		0.100
	Luvisolic	109 921	2.990	0.638	17.609		21.237
	Gleysolic	65 695	1.728	0.046	14.466		16.240
	Organic	242 592	38.305	37.941	1.480		77.726
	Sub-total		134.172	147.749	34.488		316.409
	F - Boreal B.	248 396	0.067	0.070			0.137
	Boreal F.	410 432	0.431	0.464			0.895
	G.L.-Acad.	144 468	0.071	0.075			0.146
	Grass Agr.	64 037	0.001	0.001			0.002
	Sub-total		0.570	0.610			1.180
	W - Boreal B.	248 396			0.614	0.032	0.646
	Boreal F.	410 432			2.044	0.111	2.155
	G.L.-Acad.	144 468			2.453	0.133	2.586
	Grass Agr.	64 037			12.833	0.698	13.531
	Sub-total				17.944	0.974	18.918
	L - Boreal B.	248 396	0.047	2.573			2.620
	Boreal F.	410 432	0.160	8.500			8.660
	G.L.-Acad.	144 468	0.078	4.148			4.226
	Grass Agr.	64 037	0.043	2.298			2.341
	Sub-total		0.328	17.519			17.847
	Total		135.070	165.878	52.432	0.974	354.354

TABLE 31 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- MANITOBA

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Man.	S - Chernozemic	87 768	9.426	0.228	35.818		45.472
	Luvisolic	94 889	2.581	0.550	15.201		18.332
	Regosolic	2 181	0.015	0.001	0.009		0.025
	Gleysolic	5 934	0.156	0.004	1.307		1.467
	Organic	189 968	29.996	29.711	1.159		60.866
	Podzolic	120 989	27.271	33.006	0.242		60.519
	Brunisolic	1 547	0.073	0.031	0.006		0.110
	Rockland	7 745	0.039	0.002	0.008		0.049
	Sub-total		69.555	63.533	53.750		186.838
	F - Boreal B.	184 788	0.091	0.096			0.187
	Boreal F.	257 589	0.505	0.538			1.043
	Aspen P.	44 288	0.043	0.046			0.089
	Grass Agr.	17 803					
	G.L.-Acad.	4 763	0.006	0.006			0.012
	Sub-total		0.645	0.686			1.331
	W - Boreal B.	184 788			0.456	0.024	0.480
	Boreal F.	257 589			1.283	0.070	1.353
	Aspen P.	44 288			1.677	0.091	1.768
	Grass Agr.	17 803			3.568	0.194	3.762
	G.L.-Acad.	4 763			0.081	0.004	0.085
	Sub-total				7.065	0.383	7.448
	L - Boreal B.	184 788	0.035	1.914			1.949
	Boreal F.	257 589	0.100	5.335			5.435
	Aspen P.	44 288	0.027	1.469			1.496
	Grass Agr.	17 803	0.012	0.639			0.651
	G.L.-Acad.	4 763	0.003	0.137			0.140
	Sub-total		0.177	9.494			9.671
	Total		70.377	73.713	60.815	0.383	205.288

TABLE 32 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- SASKATCHEWAN

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Sask.	S - Chernozemic	196 964	21.154	0.512	80.381		102.047
	Luvisolic	89 920	2.446	0.522	14.405		17.373
	Podzolic	179 077	40.364	48.852	0.358		89.574
	Organic	25 718	4.061	4.022	0.157		8.240
	Rockland	3 069	0.015	0.001	0.003		0.019
	Regosolic	9 794	0.066	0.004	0.045		0.115
	Solonetzic	11 556	0.519	0.141	0.106		0.766
	Gleysolic	1 378	0.036	0.001	0.303		0.340
	Sub-total		68.661	54.005	95.758		218.474
	W - Aspen P.	75 205			2.847	0.155	3.002
	Grass Agr.	53 208			10.663	0.580	11.243
	Boreal F.	264 334			1.316	0.071	1.387
	Boreal B.	47 163			0.116	0.004	0.120
	Sub-total				74.942	0.810	15.752
	L - Aspen P.	75 205	0.047	2.494			2.541
	Grass Agr.	53 208	0.036	1.909			1.945
	Boreal F.	264 334	0.103	5.474			5.577
	Boreal B.	47 163	0.009	0.489			0.498
	Sub-total		0.195	10.366			10.561
	F - Aspen P.	75 205	0.074	0.078			0.152
	Grass Agr.	53 208	0.001	0.001			0.002
	Boreal F.	264 334	0.518	0.552			1.070
	Boreal B.	47 163	0.023	0.025			0.048
	Sub-total		0.616	0.656			1.272
	Total		69.472	65.027	110.700	0.810	246.009

TABLE 33 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- ALBERTA

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Alta.	S - Chernozemic	126 161	13.501	0.328	51.479		65.308
	Solonetzic	61 383	2.755	0.749	0.565		4.069
	Regosolic	12 680	0.086	0.005	0.058		0.103
	Luvisolic	202 958	5.521	1.199	32.474		39.194
	Podzolic	8 831	1.987	2.411	0.018		4.416
	Brunisolic	10 688	0.502	0.213	0.044		0.759
	Gleysolic	28 815	0.757	0.020	6.339		7.116
	Organic	120 953	19.111	18.870	0.737		38.718
	Rockland	45 174	0.226	0.014	0.046		0.286
	Sub-total		44.446	23.809	91.760		160.015
	F - Grass Agr.	89 657	0.002	0.002			0.004
	Coastal Mt.	43 629	0.021	0.023			0.044
	Aspen P.	72 821	0.071	0.076			0.147
	Boreal F.	407 217	0.798	0.851			1.649
	Tundra	2 650					
	Boreal B.	2 393	0.001	0.001			0.002
	Sub-total		0.893	0.953			1.846
	W - Grass Agr.	89 657			17.931	0.977	18.908
	Coastal Mt.	43 629			0.740	0.041	0.781
	Aspen P.	72 821			2.759	0.150	2.909
	Boreal F.	407 217			2.028	0.110	2.138
	Tundra	2 650			0.004		0.004
	Boreal B.	2 393			0.006		0.006
	Sub-total				23.468	1.278	24.746

TABLE 33 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N $\times 10^6$ /yr)
- ALBERTA (Cont'd.)

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
Alta.	L - Grass Agr.	89 657	0.059	3.218			3.277
	Coastal Mt.	43 629	0.012	0.625			0.637
	Aspen P.	72 821	0.045	2.414			2.459
	Boreal F.	407 217	0.159	8.434			8.593
	Tundra	2 650		0.007			0.007
	Boreal B.	2 393		0.025			0.025
	Sub-total		0.275	14.723			14.998
	Total		45.614	39.485	115.228	1.278	201.605

TABLE 34 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- BRITISH COLUMBIA

Province	Emission Source	Area (km ²)	Species or Compound Class				Total
			N ₂ O	NO _x	NH ₃	Amines	
B.C.	S - Podzolic	178 641	40.266	48.733	0.357		89.356
	Luvisolic	240 220	6.534	1.417	38.435		46.386
	Brunisolic	126 627	5.951	2.533	0.519		9.003
	Rockland	235 002	1.175	0.071	1.434		2.680
	Ice	37 086					
	Gleysolic	5 386	0.142	0.004	1.186		1.332
	Chernozemic	21 156	2.272	0.055	8.634		10.961
	Solonetzic	967	0.043	0.012	0.009		0.064
	Regosolic	1 931	0.013	0.001	0.009		0.024
	Organic	39 178	6.186	6.127	0.239		12.552
	Sub-total		62.582	58.953	50.822		172.357
	L - Tundra	147 060	0.007	0.400			0.407
	Coastal Mt.	541 346	0.146	7.760			7.906
	Boreal F.	143 639	0.027	3.046			3.073
	Sub-total		0.180	11.206			11.386
	F - Tundra	149 060					
	Coastal Mt.	541 346	0.254	0.281			0.535
	Boreal F.	143 639	0.288	0.300			0.588
	Sub-total		0.542	0.581			1.123
	W - Tundra	149 060			0.244	0.013	0.257
	Coastal Mt.	541 346			9.197	0.498	9.695
	Boreal F.	143 639			0.715	0.039	0.754
	Sub-total				10.156	0.550	10.706
	Total		63.304	70.740	60.978	0.550	195.572

TABLE 35 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- NORTHWEST TERRITORIES

Territory	Emission Source	Area (km ²)	Species or Compound Class				
			N ₂ O	NO _x	NH ₃	Amines	Total
NWT	S - Podzolic	76 377	17.182	20.851	0.153		38.186
	Brunisolic	393 736	18.506	7.875	1.614		27.995
	Regosolic	2 031 776	13.606	0.813	9.346		23.765
	Gleysolic	64 554	1.698	0.045	14.202		15.945
	Organic	283 839	44.847	44.279	1.731		90.857
	Rockland	189 293	0.947	0.057	0.190		1.194
	Sub-total		96.786	73.920	27.236		197.942
F - Tundra		2 144 206					
	Boreal B.	741 370	0.363	0.385			0.748
	Boreal F.	154 000	0.302	0.322			0.624
	Sub-total		0.665	0.707			1.372
W - Tundra		2 144 206					
	Boreal B.	741 370			3.559	0.194	3.753
	Boreal F.	154 000			1.831	0.100	1.931
	Sub-total				0.767	0.042	0.809
L - Tundra		2 144 206					
	Boreal B.	741 370	0.107	5.832			5.939
	Boreal F.	154 000	0.141	7.680			7.821
	Sub-total		0.060	3.189			3.249
Total			97.759	91.328	33.393	0.336	222.816

TABLE 36 ESTIMATED ANNUAL EMISSIONS OF NITROGEN COMPOUNDS (kg N x 10⁶/yr)
- YUKON

Territory	Emission Source	Area ₂ (km ²)	Species or Compound Class				
			N ₂ O	NO _x	NH ₃	Amines	Total
Yukon	S - Brunisolic	352 773	16.544	7.040	1.446		25.030
	Regosolic	57 918	0.388	0.023	0.266		0.677
	Gleysolic	21 061	0.554	0.015	4.633		5.202
	Rockland	94 775	0.474	0.028	0.095		0.597
	Sub-total		17.960	7.106	6.440		31.506
	F - Tundra	147 828					
	Boreal B.	71 263	0.035	0.037			0.072
	Boreal F.	307 437	0.603	0.642			1.245
	Sub-total		0.638	0.679			1.317
	W - Tundra	147 828					
	Boreal B.	71 263			0.244	0.013	0.257
	Boreal F.	307 437			0.176	0.010	0.186
	Sub-total				1.529	0.083	1.612
					1.949	0.106	2.055
	L - Tundra	147 828	0.007	0.400			0.407
	Boreal B.	71 263	0.014	0.738			0.752
	Boreal F.	307 437	0.120	6.358			6.478
	Sub-total		0.141	7.496			7.637
	Total		18.739	15.281	8.389	0.106	42.515

The most recent and widely accepted global budget for nitrogen compounds emitted into the atmosphere appears to be that proposed by Soderlund and Svensson (1976). Terrestrial flux ratios derived from the global nitrogen schematic shown by these authors (p. 27) are:

$$\begin{array}{ccccc} (\text{N}_2/\text{N}_2\text{O}) - \text{N} & : & \text{NO}_x - \text{N} & : & (\text{NH}_3/\text{NH}_4) - \text{N} \\ 1.4 & : & 1.0 & : & 2.4 \end{array}$$

But, 25 to 30% of the global NO_x flux estimated by Soderlund and Svensson (1976) was attributed to anthropogenic sources. Moreover, on the basis of data presented by Van Cleemput *et al.* (1976), approximately 70% of the $\text{N}_2/\text{N}_2\text{O}$ emitted is N_2 . Flux ratios of nitrogen gases provided by Soderlund and Svensson (1976) amended to include only natural sources translate to:

$$\begin{array}{ccccc} \text{N}_2\text{O} - \text{N} & : & \text{NO}_x - \text{N} & : & (\text{NH}_3/\text{NH}_4) - \text{N} \\ 1.0 & : & 1.7 & : & 5.8 \end{array}$$

Global flux ratios determined by Robinson and Robbins (1970), amended to discount N_2O flux from marine environments and shown below, are similar:

$$\begin{array}{ccccc} \text{N}_2\text{O} - \text{N} & : & \text{NO}_x - \text{N} & : & \text{NH}_3 - \text{N} \\ 1.0 & : & 1.8 & : & 7.4 \end{array}$$

Flux ratios presented above differ from those determined in the present study in that they show a stronger representation of $(\text{NH}_3/\text{NH}_4) - \text{N}$ flux. Terrestrial global flux ratios proposed by Rasmussen *et al.* (1975) of approximately:

$$\begin{array}{ccccc} \text{N}_2\text{O} - \text{N} & : & \text{NO}_x - \text{N} & : & \text{NH}_3 - \text{N} \\ 1.0 & : & 1.8 & : & 1.1 \end{array}$$

on the other hand, are in closer agreement with those determined in this study. Average terrestrial global flux ratios from the above authors are:

$$\begin{array}{ccccc} \text{N}_2\text{O} - \text{N} & : & \text{NO}_x - \text{N} & : & \text{NH}_3 - \text{N} \\ 1.0 & : & 1.8 & : & 3.6 \end{array}$$

9.2 Marine Zone Emissions

Zafiriou *et al.* (1980) suggested that NO is emitted into the atmosphere from tropical marine waters, but no flux estimates are available, nor is there any indication that similar processes occur in temperate or polar zones. It has also been suggested that marine waters may liberate NH_3 into the atmosphere (Soderlund and Svensson 1976). But

again no data are available. The only nitrogenous gas other than N_2 known to be emitted from marine environments in significant quantities is N_2O .

N_2O flux estimates from Canadian marine waters derived in Section 4.1.6 are as follows ($g\ N_2O-N/m^2/yr$):

Arctic Regions	0.029
Pacific Regions	0.101
Atlantic Region - north	0.059
- south	0.084

There are no data in the literature to indicate the relative strengths of fluxes from near shore and open waters. All waters within a given region are therefore assumed to liberate N_2O at the above rates.

Estimates of annual N_2O emissions from Canadian waters are summarized in Table 37.

TABLE 37 ESTIMATED ANNUAL EMISSIONS OF NITROGENOUS COMPOUNDS FROM CANADIAN MARINE ENVIRONMENTS ($kg\ N \times 10^6/yr$)

Marine Zone	Area (km^2)	$N_2O - N$
Arctic	2 962 200	85.95
Pacific	156 250	15.78
Atlantic - north	111 250	6.57
Atlantic - south	375 650	31.53

GLOSSARY

Definitions of Terms as Used in this Report

Aspen Parkland	-	open aspen forests separating grassland and boreal forest zones of the Prairies
Atmospheric fate	-	the pathway by which a particular species is removed from the troposphere, which includes chemical reactions, precipitative scavenging, adherence to particulates, transport to the stratosphere and other mechanisms
Biomass	-	the amount of organic matter accumulated as a result of net productivity
Biome	-	a major ecological community such as boreal forest or grassland
Boreal Forest	-	vast expanse of closed coniferous forest extending coast to coast across the centre of Canada
Boreal Forest - Barrens	-	open coniferous forests separating the closed boreal forest to the south and tundra regions to the north
Coastal - Mountain Forest	-	primarily coniferous forests of British Columbia and mountainous portions of western Alberta
Emission rate	-	amount of gases and particulates discharged into the atmosphere per unit time
Flux	-	rate of discharge of gases and particulates across a given surface area per unit of time
Grassland - Agriculture	-	Prairie grasslands and areas cleared for agriculture in southern Canada
Great Lakes - Acadian Forest	-	mixed forest regions of southern and central Ontario, southern Quebec and the Maritimes
Hydrogen abstraction	-	the removal of a hydrogen atom from a given molecule by any number of radicals and/or compounds such as HO•

- Hydrogen substitution - removal of a hydrogen atom from a given molecule followed by substitution of an atom or group of atoms
- Photochemical-oxidation - oxidation processes requiring precursors produced by radiant energy
- Photodissociation - dissociation under the influence of radiant energy
- Photolysis - chemical decomposition by the action of radiant energy
- Radical - an atom or group of atoms replaceable by a single atom
- Reactivity - the rate of disappearance of one of the reactants of a chemical system; for the purpose of this report reactivities of various compounds with atmospheric reactants such as hydroxyl radicals (HO) and ozone molecules (O₃) are measured relative to that of methane such that the reactivity of methane with any particular atmospheric reactant is given a value of unity
- Residence Time - the shortest lifetime of any given reactant determined according to the following formulation
- $$\gamma_A = \frac{1}{k_{AB} (C_B)}$$
- where γ_A = lifetime of species A
- K_{AB} = rate constant for reaction of A and B
- (C_B) = average concentration of species B
- Tundra - the northern treeless zone

Units

mass:	μg	=	microgram	=	10^{-6} grams
	mg	=	milligram	=	10^{-3} grams
	kg	=	kilogram	=	10^3 grams
	t	=	tonne	=	10^6 grams
	Tg	=	teragram	=	10^{12} grams
	gN	=	grams nitrogen		
volume:	nL	=	nanolitre	=	10^{-9} litres

Selected Chemical Nomenclature and Symbols

O	-	oxygen atom
$\text{O} (^3\text{p})$	-	ground state oxygen atom
$\text{O} (^1\text{D})$	-	excited state oxygen atom
$\text{O}_2 (^1\Delta)$	-	excited state molecular oxygen
O_3	-	ozone
HO	-	hydroxyl radical
NO	-	nitric oxide
$h\nu$	-	solar photons
Fct. of λ	-	function of wavelength
R	-	generalized portion of an organic molecule to which an atom or group of atoms is attached
M	-	catalyst

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